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NUMBER 1

## ON POTENTIAL MOMENTUM AND MOMENTUM FIELDS IN DYNAMICS<sup>1</sup>

BY W. H. WATSON<sup>2</sup>

### Abstract

Based on previous work of the writer (2) this paper deals with the specification of dynamical systems via potential momentum and momentum fields, and setting out from the continuous motion formally identical with the meson→electron transformation, opens the study of systems of motions of a single particle defined by

$$\frac{dP_\rho}{ds} = F_{\rho\sigma} \frac{dx_\sigma}{ds}$$

where  $F_{\rho\sigma}$  is not an antisymmetric tensor. Fields which, in addition to the usual electromagnetic effects, change the rest-mass of a particle moving under their action, and which are caused by the creation or destruction of electric charge, are proposed as the classical model for neutrino radiation.

### Introduction

The conception "potential momentum" has been introduced into dynamics through study of the equations of motion of an electrified particle in a given electromagnetic field. If the scalar potential is  $\varphi$  and the vector potential is  $\mathbf{a}$ , then for a charge  $e$  the potential momentum is  $e\mathbf{a}$  corresponding to the potential energy  $e\varphi$ , the units being suitably chosen. So long as we are dealing with a Hamiltonian system of a single particle, it is formally possible to describe the motion as motion in a given electromagnetic field; but when we come to deal with a Hamiltonian system of two particles, in addition to electromagnetic forces between the particles, other possible modes of interaction present themselves. This logical situation was pointed out by the present writer a few years ago (2). The method adopted was to define the system by means of a potential momentum field, but no particular cases of the application of the method were considered. With the general idea that some correspondence might be established between such a field and a neutrino field in quantum mechanics, when the former does not exhibit electromagnetic characteristics, it has seemed of interest to examine some of the possible systems of particle motions to which one is led by considering systems defined in the manner referred to.

In §1, we shall for simplicity deal with the motion of a system of particles in one dimension, treating dynamics in terms of the Newtonian principle of relativity. In this and the succeeding section, there is brought out clearly the part played in the definition of the system by choice of a system of reference

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for describing the motion. It will be observed that with the systems proposed for study, the description in terms of potential momentum is more appropriate than that in terms of potential energy, which must be redefined for each choice of the constants of integration by the other method. Indeed the potential momentum method gives a choice of reference system that the other method does not offer. In §2 the corresponding motions for a system of two or three particles in three dimensions, electromagnetic interactions between the particles being left out of account, are discussed, and some of the properties of the momentum field are exhibited. In §3 we turn to the motion of a single particle, taking into account special relativity in order to deduce the transformation of energy and momentum for a particle such as a meson changing into an electron with the emission of a neutrino of zero rest-mass. This transformation is equivalent to a Lorentz transformation with the determining velocity constant in magnitude and the equations of transformation modified by a constant factor which introduces a change of scale in addition to the rotation of axes of the ordinary Lorentz transformation. The corresponding continuous transformation is then set up, and we are led to introduce the motion of a particle in a field specified by a tensor playing in the equations of motion the same formal role as the electromagnetic field tensor but with this difference—it is not required to be an antisymmetric tensor. The equations of motion of a particle in such a field cannot in general be expressed in Hamiltonian form, but when the field tensor is *symmetric* can be put in what we have called anti-Hamiltonian form, in which anti-commuting brackets play in some respects the part of the Poisson expressions of Hamiltonian dynamics. The non-Hamiltonian systems of particle motions in such fields are treated by two methods in §4, while in §5 some properties of the fields themselves are investigated. In Subsection (iv) of §5, will be found a brief discussion of a possible continuous representation of a neutrino field. In this representation the tensor specifying the field differs from an electromagnetic field tensor only in the presence of non-zero diagonal components which, it is shown, alter in general the rest-mass of a particle acted on by the field. The singularities acting as sources of fields with non-zero diagonal components are points where electric charge is being created or destroyed. The investigation is not carried farther in the present work to make contact with current nuclear theory.

### §1. Simple Systems: Motion in One Dimension

The simplest system we can propose is one of two particles free to move on a straight line according to the system of equations

$$m_1 \ddot{x}_1 = f \dot{x}_2 \quad m_2 \ddot{x}_2 = -f \dot{x}_1 \quad (1)$$

where  $f$  is a numerical constant. The integrals of momentum and energy are respectively,

$$m_1 \dot{x}_1 + m_2 \dot{x}_2 + f(x_1 - x_2) = P \quad (2)$$

and

$$\frac{1}{2} m_1 \dot{x}_1^2 + \frac{1}{2} m_2 \dot{x}_2^2 = E \quad (3)$$

where  $P$  and  $E$  are constants. Here the quantity  $f(x_1 - x_2)$  plays the role

potential momentum. This system does not conform to Newton's third law of motion, unless we conceive of the system as a whole acted on by an external force which does no work on it. From Equation (2) it is obvious that if the motion is referred to an origin moving with the acceleration  $\ddot{x}_0$  given by

$$M\ddot{x}_0 = f(\dot{x}_2 - \dot{x}_1), \quad M = m_1 + m_2 \quad (4)$$

Equations (2) and (3) are transformed into

$$m_1\dot{\xi}_1 + m_2\dot{\xi}_2 = P' \quad (5)$$

and

$$\frac{1}{2}m\dot{\xi}_1^2 + \frac{1}{2}m\dot{\xi}_2^2 + \frac{f}{2M}(\xi_2 - \xi_1)^2 + \frac{P'f}{2M}(\xi_2 - \xi_1) = E' \quad (6)$$

where  $P'$  and  $E'$  are constants. The transformation of axes results in the conversion of potential momentum into potential energy. According to classical methods the system would be defined by Equation (6), i.e., relatively to the system of axes in which the centre of mass is not accelerated. The system of motions so defined is very much more restricted than that defined by (1) which allow  $P'$  to be a variable, whereas (6) requires  $P'$  to be a given constant of the system. The motion, of course, is a vibration:

$$\begin{aligned} x_1 &= B/f + \frac{\sqrt{Em_2}}{f} \cos(nt + \epsilon) & n^2 &= f^2/m_1m_2 \\ x_2 &= -A/f - \frac{\sqrt{Em_1}}{f} \sin(nt + \epsilon) & A + B &= P \end{aligned} \quad (7)$$

or, in the other system of reference

$$\left. \begin{aligned} \xi_2 &= \frac{P't}{M} + \frac{B}{M} - \frac{P'm_1}{Mf} + \frac{Am_1}{M} \cos(nt + \epsilon) \\ \xi_1 &= \frac{P't}{M} + \frac{B}{M} + \frac{P'm_2}{Mf} - \frac{Am_2}{M} \cos(nt + \epsilon) \\ \xi_1 - \xi_2 &= \frac{P'}{f} - A \cos(nt + \epsilon) \end{aligned} \right\} \quad (8)$$

The two particles are carried along with the speed  $P'/M$ , and their relative distance executes simple harmonic motion about  $P'/f$ . On the other hand, with respect to (7) corresponding to Equations (1), we may speak of the particles as placed in the constant field  $f$ , the effect of which may be represented in the  $x_1x_2$ -plane by the motion of a charged particle acted on by a uniform magnetostatic field of strength  $f/e$  normal to the plane,  $e$  being the charge on the particle.

The next most simple system is that of three particles free to move on a line with the equation system:

$$\begin{aligned} m_1\ddot{x}_1 &= a_{12}\dot{x}_2 - a_{31}\dot{x}_3 \\ m_2\ddot{x}_2 &= -a_{12}\dot{x}_1 + a_{23}\dot{x}_3 \\ m_3\ddot{x}_3 &= a_{31}\dot{x}_1 - a_{23}\dot{x}_2 \end{aligned} \quad (9)$$

where  $a_{12}$ ,  $a_{23}$ ,  $a_{31}$  are numerical constants. The velocities  $\dot{x}_1$ ,  $\dot{x}_2$ ,  $\dot{x}_3$  are all solutions of

$$\ddot{y} + p^2\dot{y} = 0 \quad \text{where} \quad p^2 = \Sigma \frac{a_{23}^2}{m_2m_3} \quad (10)$$

Hence

$$\dot{x}_1 = \frac{A_1}{p^2} + C_1 \cos(pt + \epsilon_1) \quad (11)$$

where  $A_1$ ,  $C_1$ , and  $\epsilon_1$  are constants. Similar expressions hold for  $\dot{x}_2$  and  $\dot{x}_3$ , and of course

$$\frac{a_{23}}{A_1} = \frac{a_{31}}{A_2} = \frac{a_{12}}{A_3} \quad (12)$$

and only four of  $C_1$ ,  $C_2$ ,  $C_3$ ,  $\epsilon_1$ ,  $\epsilon_2$ ,  $\epsilon_3$ , are independent in virtue of (9).

This system has the remarkable property that in addition to the oscillation, it has in general a motion dispersing the particles. Only if  $a_{12} = a_{23} = a_{31}$  will the particles remain together. Consequently if the  $a$ 's were made *slowly* varying functions of the time, we could bring the particles together, keep them oscillating close to each other with the  $a$ 's all equal, and as the  $a$ 's started to differ the system would disperse; but of course such a process would require special choice of the initial conditions of the motion as well as of the dependence of the  $a$ 's on the time. Throughout, it may be noted, the kinetic energy remains constant, whereas the momentum of the whole system is a linear function of the relative separations of the pairs of particles, i.e., the system has potential momentum.

If the system consists of four particles, it is readily shown that the condition (in notation analogous to that employed above)

$$a_{12} a_{34} + a_{23} a_{14} + a_{31} a_{24} = 0 \quad (13)$$

is necessary to permit dispersal of the system, and if it is not fulfilled, there are two non-zero frequencies of oscillation.

Provided that we exclude the possibility of dispersal of the system, which would prevent solutions by continuous functions of the variable naming the particles in place of the indices used previously, we could apply the method to a linear continuum; the system of equations of motion becomes the integro-differential equation

$$\sigma(s)\ddot{x}(s) = \int_0^1 G(s, s')\dot{x}(s')ds \quad (14)$$

where  $G(s, s') = -G(s', s)$  and is independent of  $x(s)$  and  $t$ . The potential momentum is given by

$$\int_0^1 \int_0^1 G(s', s)[\dot{x}(s') - \dot{x}(s)]ds'ds = \mathfrak{W} \quad (15)$$

and

$$\int_0^1 \sigma(s)\dot{x}(s)ds + \mathfrak{W} = P \text{ (a constant)} \quad (16)$$

The energy equation is

$$\int_0^1 \frac{1}{2}\sigma(s)[\dot{x}(s)]^2 ds = E \quad (17)$$

## §2. Three Dimensional Motion of a System of Particles

Before proceeding to discuss the motion of a system of particles in three dimensions, we should reconsider the method by which the systems in question are to be defined (1, p. 126). We set out from the differential form\*

$$\omega = \sum_i \sum_r P_{ir} dx_{ir} - W dt \quad (18)$$

where  $i = 1, 2, \dots, n$  refers to the particle and  $r = 1, 2, 3$ .

Since for the present we intend to exclude forces of electromagnetic type, we must have in the derived form  $\omega'$  no terms in the symbolic differentials  $dx_{ir}, dx_{is}$  or  $dx_{ir} dt$ , that is

$$\frac{\partial P_{ir}}{\partial x_{is}} - \frac{\partial P_{is}}{\partial x_{ir}} = 0 \quad \text{and} \quad \frac{\partial P_{ir}}{\partial t} + \frac{\partial W}{\partial x_{ir}} = 0 \quad (19)$$

The symbolic form adjoint to the form  $\omega'$  so reduced is

$$\Omega = \sum_{i \neq j} \left( \frac{\partial P_{ir}}{\partial x_{is}} - \frac{\partial P_{is}}{\partial x_{ir}} \right) \prod_{s \neq r} dx_{is} \prod_{r \neq s} dx_{ir} dt \prod_{\substack{k \neq i, j \\ u}} dx_{ku} \quad (20)$$

summed over all pairs  $(ir), (is)$ .

For simplicity let us restrict ourselves to two particles, then

$$\Omega = \left( \frac{\partial P_{11}}{\partial x_{21}} - \frac{\partial P_{21}}{\partial x_{11}} \right) dx_{12} dx_{13} dx_{22} dx_{23} dt + \left( \frac{\partial P_{11}}{\partial x_{22}} - \frac{\partial P_{22}}{\partial x_{11}} \right) dx_{12} dx_{13} dx_{23} dx_{21} dt \\ + 7 \text{ similar terms} \quad (21)$$

The derived form  $\Omega'$  is built up from terms of the type

$$\left\{ \frac{\partial}{\partial x_{21}} \text{div}_1(P_{11}, P_{12}, P_{13}) - \nabla_1^2 P_{11} \right\} dx_{11} dx_{13} dx_{21} dx_{22} dx_{23} dt \quad (22)$$

Now since no electromagnetic interactions are allowed, we may write

$$\begin{aligned} (P_{11}, P_{12}, P_{13}) &= \text{grad } U_1 \\ (P_{21}, P_{22}, P_{23}) &= \text{grad } U_2 \end{aligned} \quad (23)$$

where  $U_1$  and  $U_2$  are functions of the co-ordinates of both particles and if

$$\varphi = U_1 - U_2 \quad (24)$$

$$\frac{\partial P_{11}}{\partial x_{21}} - \frac{\partial P_{21}}{\partial x_{11}} = \frac{\partial^2 \varphi}{\partial x_{11} \partial x_{21}}$$

and similarly all the other coefficients of  $\omega'$  are mixed second derivatives of  $\varphi$ .

The term in  $\Omega'$  quoted above becomes

$$\frac{\partial}{\partial x_{21}} \{ \nabla_1^2 \varphi \} dx_{12} dx_{13} dx_{21} dx_{22} dx_{23} dt.$$

Now since  $\Omega'' \equiv 0$ , we have

$$\nabla_2^2 \nabla_1^2 \varphi = 0 \quad (25)$$

When the separate times are introduced for the different particles the Laplacian operators will be replaced by the d'Alembertian ones, and  $\varphi$  will be a function of the  $t$ 's as well as of the  $x$ 's. We shall not consider this case, but note it for future reference.

\* It may be noticed that if we wish to use the methods of special relativity, the term  $W dt$  will have to be written  $\sum_i T_i dt_i$ , the particles being assigned separate times.

Let us now consider a system of two particles  $(x, y, z; x', y', z')$  acted on by a field defined by  $\varphi$ , and suppose that  $\varphi$  is a function of the relative co-ordinates only. For brevity write

$$\frac{\partial^2 \varphi}{\partial x \partial x'} = \varphi_{11}, \quad \frac{\partial^2 \varphi}{\partial x \partial y'} = \varphi_{12} = \frac{\partial^2 \varphi}{\partial y' \partial x} = \frac{\partial^2 \varphi}{\partial x' \partial y} = \varphi_{21} \quad (26)$$

The equations of motion are: [see (1)]

$$\begin{aligned} m\ddot{x} &= \varphi_{11}\dot{x}' + \varphi_{12}\dot{y}' + \varphi_{13}\dot{z}' \\ m\ddot{y} &= \varphi_{21}\dot{x}' + \varphi_{22}\dot{y}' + \varphi_{23}\dot{z}' \\ m\ddot{z} &= \varphi_{31}\dot{x}' + \varphi_{32}\dot{y}' + \varphi_{33}\dot{z}' \end{aligned} \quad (27)$$

or

$$m\ddot{\mathbf{r}} = A\dot{\mathbf{r}}' \quad (\mathbf{r} = (x, y, z)) \quad (28)$$

where  $A$  is the matrix of coefficients in (27). For the second particle

$$m'\ddot{\mathbf{r}}' = -A^*\dot{\mathbf{r}} \quad (28')$$

where  $A^*$  is the transponent of  $A$ .

We have from (28)

$$\begin{aligned} M\ddot{X} &= m\ddot{x} + m'\ddot{x}' = \varphi_{11}(\dot{x}' - \dot{x}) + \varphi_{12}(\dot{y}' - \dot{y}) + \varphi_{13}(\dot{z}' - \dot{z}) \\ &= \frac{d}{dt}(\varphi_1) \end{aligned}$$

where

$$\varphi_1 = \frac{\partial \varphi}{\partial x} = -\frac{\partial \varphi}{\partial x'}$$

Thus

$$M\dot{X} = m\dot{x} + m'\dot{x}' = \varphi_1 + \text{constant}. \quad (29)$$

Therefore  $\left\{ \frac{\partial \varphi}{\partial x'}, \frac{\partial \varphi}{\partial y'}, \frac{\partial \varphi}{\partial z'} \right\}$  is the potential momentum of the system. Further we have

$$\begin{aligned} m\ddot{\xi} &= m(\ddot{x} - \ddot{X}) = \frac{1}{M} \left\{ \varphi_{11}(m'\dot{x}' + m\dot{x}) + \varphi_{12}(m'\dot{y}' + m\dot{y}) + \varphi_{13}(m'\dot{z}' + m\dot{z}) \right\} \\ &= \frac{1}{M} \left\{ \varphi_{11}(C_1 + \varphi_1) + \varphi_{12}(C_2 + \varphi_2) + \varphi_{13}(C_3 + \varphi_3) \right\} \\ &= -\frac{\partial}{\partial \xi} \frac{1}{M} \left( \frac{1}{2}(\varphi_1^2 + \varphi_2^2 + \varphi_3^2) + C_1\varphi_1 + C_2\varphi_2 + C_3\varphi_3 \right). \end{aligned} \quad (30)$$

The original system defined via the potential momentum  $-(\varphi_1, \varphi_2, \varphi_3)$  together with the particular values  $(C_1, C_2, C_3)$  of the additive constants of momentum is equivalent to the system of two particles with the potential energy

$$V = \frac{1}{2M} \left\{ (\varphi_1 + C_1)^2 + (\varphi_2 + C_2)^2 + (\varphi_3 + C_3)^2 \right\}. \quad (31)$$

If  $\varphi$  is a function not merely of the relative co-ordinates of the particles but more particularly of their relative distance  $R$  only, then since on account of (25)

$$\frac{1}{R} \frac{d^4}{dR^4}(R\varphi) = 0 \quad R^2 = (x' - x)^2 + (y' - y)^2 + (z' - z)^2 \quad (32)$$



$\varphi$  is restricted to have one of the forms  $R^{-1}$ ,  $R$ ,  $R^2$  or a linear combination of them. When  $\varphi = aR^2$  the  $\varphi_{,n}$  are all constant and equal.

Let us deal with the case where all the  $\varphi_{,n}$  are constants independent of  $x, y, z, x', y', z'$ , and  $t$ .

$$m\ddot{\mathbf{r}} = A\dot{\mathbf{r}}' \quad m'\dot{\mathbf{r}}' = -A^*\dot{\mathbf{r}} \quad (33)$$

Thus

$$mm'\ddot{\mathbf{r}} = -AA^*\dot{\mathbf{r}}$$

or

$$mm'\ddot{\mathbf{r}} = -AA^*(\mathbf{r} + \alpha) \quad (34)$$

where  $\alpha$  is a constant vector. This equation informs us that there are in general three independent frequencies of vibration about the position defined by the vector  $\alpha$ .

A system of three particles subject to forces of the same type is governed by the system of equations

$$\left. \begin{aligned} m_1\ddot{\mathbf{r}}_1 &= A_{12}\dot{\mathbf{r}}_2 + A_{13}\dot{\mathbf{r}}_3 \\ m_2\ddot{\mathbf{r}}_2 &= A_{21}\dot{\mathbf{r}}_1 + A_{23}\dot{\mathbf{r}}_3 \\ m_3\ddot{\mathbf{r}}_3 &= A_{31}\dot{\mathbf{r}}_1 + A_{32}\dot{\mathbf{r}}_2 \end{aligned} \right\} \quad (35)$$

where the  $A$ 's are matrices with three rows and three columns and  $A_{21} = -A_{12}^*$  etc.

On integration when the matrix elements are constants, we obtain the momentum equation

$$m_1\dot{\mathbf{r}}_1 + m_2\dot{\mathbf{r}}_2 + m_3\dot{\mathbf{r}}_3 = (A_{31} + A_{21})\mathbf{r}_1 + (A_{12} + A_{32})\mathbf{r}_2 + (A_{13} + A_{23})\mathbf{r}_3 + \mathbf{p} \quad (36)$$

where  $\mathbf{p}$  is a constant vector. The procedure for treating this system with regard to its potential momentum field follows along the lines indicated for two particles and is necessarily complicated.

### §3. Non-electromagnetic Motion of a Single Particle

We now turn to the case of a single particle and treat its motion in accordance with special relativity. As was indicated in the introduction, our intention is to look for a classical parallel to the neutrino field: we therefore note certain results following from the assumption that a particle of mass  $M$  (meson) can be transformed into a particle of mass  $m$  (electron) with the emission of a particle of zero rest-mass (neutrino).

Let  $U$  and  $v$  be the velocities of the meson and electron respectively;  $E, \epsilon$  the respective energies, and  $\mathbf{P}, \mathbf{p}$  the respective momenta. Let  $\alpha = m/M$  be the ratio of the rest-masses, and let us take the velocity of light as unity. Since in the transformation the momentum and energy are to be conserved with the aid of a particle of zero rest-mass

$$(E - \epsilon)^2 - |\mathbf{P} - \mathbf{p}|^2 = 0 \quad (37)$$

i.e.,

$$(E - \epsilon)^2 = \mathbf{P}^2 - 2\mathbf{P} \cdot \mathbf{p} + \mathbf{p}^2 \quad (38)$$

or

$$M^2 + m^2 = \frac{2Mm(1 - U \cdot v)}{\sqrt{(1 - U^2)(1 - v^2)}} \quad (39)$$

Now the velocity  $\gamma$  of the electron with respect to a system moving with the velocity  $U$  of the meson is

$$\gamma = \frac{\beta[(v \cdot U_0)U_0 - U] - (v \times U_0) \times U_0}{\beta(1 - v \cdot U)} \quad (40)$$

where

$$\beta = (1 - U^2)^{-1/2} \quad U_0 = U/|U|$$

Hence

$$\gamma^2 = 1 - \frac{(1 - U^2)(1 - v^2)}{(1 - v \cdot U)^2} \quad (41)$$

and

$$M^2 + m^2 = \frac{2Mm}{\sqrt{1 - \gamma^2}}$$

$$\therefore \sqrt{1 - \gamma^2} = \frac{2\alpha}{1 + \alpha^2} \quad |\gamma| = \frac{1 - \alpha^2}{1 + \alpha^2} \quad (42)$$

The magnitude of this relative velocity is independent of the direction of neutrino emission.

We shall now deduce the simple transformation scheme by which the energy and momentum of the electron are derived from the corresponding quantities for the meson.

Now

$$\gamma \cdot P = E(\gamma \cdot U) = E \frac{(v \cdot U - U^2)}{1 - v \cdot U} \quad (43)$$

hence

$$E + \gamma \cdot P = E \frac{(1 - U^2)}{1 - v \cdot U}$$

$$\sqrt{1 - \gamma^2}(E + \gamma \cdot P) = E \sqrt{\frac{1 - U^2}{1 - v^2}} = \sqrt{1 - v^2} = \frac{\epsilon}{\alpha}$$

So

$$\epsilon = \sqrt{1 - \gamma^2}(E + \gamma \cdot P) \quad (44)$$

Now

$$P = \epsilon v = \alpha E \frac{(1 + \gamma \cdot U)}{\sqrt{1 - \gamma^2}} v$$

and

$$v = \frac{(1 - \gamma^2)^{-1/2}[(U \cdot \gamma_0)\gamma_0 + \gamma] + (U \times \gamma_0) \times \gamma_0}{(1 - \gamma^2)^{-1/2}(1 + \gamma \cdot U)}$$

Thus

$$P = \alpha\{(1 - \gamma^2)^{-1/2}[(P \cdot \gamma_0)\gamma_0 + \gamma E] + (P \times \gamma_0) \times \gamma_0\} \quad (45)$$

Equations (44) and (45) show that the momentum and energy of the electron are derived from the energy and momentum of the meson by a Lorentz transformation with velocity  $-\gamma$  and modified by the scale constant  $\alpha$  as a factor of proportionality;  $\alpha$  is of course connected with  $\gamma$  through (42).

Now imagine this transformation to take place continuously according to the same law. We suppose therefore that  $\alpha$  differs from unity by a small quantity  $\eta$ ,  $\alpha = 1 - \eta$ . Then  $|\gamma| = \eta$

$$P - P = -\eta P + \eta \gamma_0 E$$

$$\epsilon - E = -\eta E + \eta \gamma_0 \cdot P$$



With  $\eta = \kappa_0 ds$ , pass to the limit

$$\lim_{ds \rightarrow 0} \frac{L t}{ds} \frac{\mathbf{p} - \mathbf{P}}{ds} = \frac{d\mathbf{P}}{ds} \quad \lim_{ds \rightarrow 0} \frac{L t}{ds} \frac{\epsilon - E}{ds} = \frac{dE}{ds}$$

and we have the system of equations of motion

$$\left. \begin{aligned} \frac{d\mathbf{P}}{ds} &= -\kappa_0 \mathbf{P} + \kappa_0 \gamma_0 E \\ \frac{dE}{ds} &= -\kappa_0 E + \kappa_0 \gamma_0 \mathbf{P} \end{aligned} \right\} \quad (46)$$

An alternative form of the equations is

$$\begin{aligned} \frac{dP_r}{ds} &= -\lambda_0 \frac{dx_r}{ds} + \lambda_r \frac{dt}{ds} \\ \frac{dE}{ds} &= -\lambda_0 \frac{dt}{ds} + \sum_r \lambda_r \frac{dx_r}{ds} \quad (r = 1, 2, 3,) \end{aligned} \quad (47)$$

The parameters  $\kappa_0$ ,  $\gamma_0$  or  $\lambda_0$ ,  $\lambda_r$  will in general be functions of  $x_r$  and  $t$ .

(i) If  $\lambda_r = \lambda_0 a_r$  ( $r = 1, 2, 3$ ) and the  $a_r$  are constants, then

$$E - \sum_r a_r P_r = \text{constant} \quad (48)$$

is an integral of (47). The component of the momentum 4-vector of the particle along a certain fixed direction in space-time is constant.

(ii) Suppose that Equations (47) may be combined in the form

$$b_0 \frac{dE}{ds} - \sum_r b_r \frac{dP_r}{ds} = \sum_r (b_0 \lambda_r + b_r \lambda_0) \frac{dx_r}{ds} - (\sum_r b_r \lambda_r + b_0 \lambda_0) \frac{dt}{ds} \quad (49)$$

so that after the proper choice of the constants  $b_r$  and  $b_0$ , the second member is integrable; we have

$$b_0 E - \sum_r b_r P_r = \text{Constant} - \varphi(x_r, t) \quad (50)$$

The function  $\varphi$  is a type of potential momentum. The conditions of integrability for (49) are

$$\left. \begin{aligned} \sum_r b_r \lambda_r + b_0 \lambda_0 &= \frac{\partial \varphi}{\partial t} \\ b_0 \lambda_r + b_r \lambda_0 &= -\frac{\partial \varphi}{\partial x_r} \end{aligned} \right\} \quad (51)$$

On account of the relation  $\lambda_0^2 = \sum_r \lambda_r^2$ ,  $\varphi$  must satisfy

$$\sum_r \lambda_r \frac{\partial \varphi}{\partial x_r} + \lambda_0 \frac{\partial \varphi}{\partial t} = 0 \quad (52)$$

Consequently if the  $\lambda$ 's are constant  $\varphi$  is the function  $\lambda_0 t - \sum_r \lambda_r x_r$ ,  $b_0 = 1$ ,  $b_r = 0$  and  $E = \text{Constant} - \varphi$ . Hence  $\varphi$  is the potential energy and is a function of the time and the co-ordinates. The components of potential momentum are  $\lambda_0 x_r - \lambda_r t$ .

(iii) From (47)

$$\frac{dt}{ds} \frac{dE}{ds} - \sum_r \frac{dx_r}{ds} \frac{dP_r}{ds} = -\lambda_0$$

hence

$$\frac{dm}{ds} = -\lambda_0 \quad (53)$$

$m$  being the rest-mass of the particle. This result is to be expected from inspection of the method by which the equations of motion were generated.

The equation system with which we have been dealing may be a particular case of the general type

$$\frac{dP_\rho}{ds} = F_{\rho\sigma} \frac{dx_\sigma}{ds} \quad (54)$$

$$\rho, \sigma = 1, 2, 3, 4, \quad P_4 = -E, \quad x_4 = t$$

which we shall examine in the next section.

#### §4. Non-Hamiltonian Systems with Potential Momentum

There are three main types based on (54) as the equations of motion:— (i)  $F_{\rho\sigma}$  an antisymmetric tensor yielding the usual electromagnetic motion in a given field, (ii)  $F_{\rho\sigma}$  a symmetric tensor, and (iii) the general case in which  $F_{\rho\sigma}$  may be written as the sum of a symmetric and an antisymmetric tensor. In (ii) and (iii) the motion differs fundamentally from that in a given electromagnetic field because of the non-vanishing diagonal components of the tensor. The system (47) is of type (iii) defined by  $F_{rr} = -\lambda_0$  ( $r = 1, 2, 3$ ),  $F_{44} = \lambda_0$ ,  $F_{r4} = -F_{4r} = \lambda_r$  (all other components vanish).

Passing from the electromagnetic case where  $F_{\mu\nu} = \varphi_{\mu\nu} - \varphi_{\nu\mu}$ ,  $\varphi_\mu$  being the potential, we consider the symmetric tensor

$$F_{\mu\nu} = A_{\mu\nu} + A_{\nu\mu} \quad (55)$$

where  $A_\mu$  is a given vector function of  $x_\mu$ . The equations (54) then become

$$\frac{dP_\rho}{ds} = \left( \frac{\partial A_\rho}{\partial x_\sigma} + \frac{\partial A_\sigma}{\partial x_\rho} \right) \frac{dx_\sigma}{ds}$$

or

$$\frac{d}{ds} (P_\rho - A_\rho) = + \frac{\partial A_\sigma}{\partial x_\rho} \frac{dx_\sigma}{ds}$$

Thus

$$\frac{d}{dt} (P_\rho - A_\rho) = + \frac{\partial A_\sigma}{\partial x_\rho} \frac{dx_\sigma}{dt} \quad (56)$$

and it must be noted that these equations are not expressible in Lagrangian form on account of the positive sign of the second member.

Write

$$P_\rho - A_\rho = p_\rho \quad \text{or} \quad P_\rho = p_\rho + A_\rho \quad (57)$$

and introduce in the case of constant rest-mass

$$Y(p_r, x_r, t) = \sqrt{m^2 + \sum_r P_r^2} + A_4 \quad (r = 1, 2, 3) \quad (58)$$

Then

$$\frac{\partial Y}{\partial p_r} = \frac{P_r}{\sqrt{m^2 + \sum_r P_r^2}} = \frac{P_r}{E} = \frac{dx_r}{dt}$$

$$\frac{\partial Y}{\partial x_r} = \sum_s \frac{P_s}{\sqrt{m^2 + \sum_r P_r^2}} \frac{\partial A_s}{\partial x_r} + \frac{\partial A_4}{\partial x_r} = \sum_s \frac{\partial A_s}{\partial x_r} \frac{dx_s}{dt} + \frac{\partial A_4}{\partial x_r} = \frac{dp_r}{dt}$$

Thus we have the equations of motion (55) and  $P_\rho = g_{\rho\rho} m \frac{dx_\rho}{ds}$  ( $g_{11} = g_{22} = g_{33} = -g_{44} = 1$ ) in the form

$$\frac{dx_r}{dt} = \frac{\partial Y}{\partial p_r}, \quad \frac{dp_r}{dt} = + \frac{\partial Y}{\partial x_r} \quad (59)$$

whereas if we had used the antisymmetric tensor  $F_{\mu\nu}$  in place of the symmetric one we should obtain the canonical equations

$$\frac{dx_r}{dt} = \frac{\partial Y}{\partial p_r}, \quad \frac{dp_r}{dt} = - \frac{\partial Y}{\partial x_r}$$

$Y$  being the Hamiltonian function. We shall speak of the system (59) as an anti-Hamiltonian system. It is obvious that even when  $Y$  does not involve  $t$  explicitly,  $Y$  is not a constant of the motion unless the field vanishes.

In order to deal with varying rest-mass we introduce

$$Z(p_\rho, x_\rho) = -\sqrt{-P_\rho P^\rho} = -\sqrt{-g_{\rho\rho} P_\rho^2} \quad (60)$$

with

$$\begin{aligned} \frac{\partial Z}{\partial p_\rho} &= \sqrt{\frac{g_{\rho\rho} P_\rho}{-g_{\rho\rho} P_\rho^2}} = \frac{dx_\rho}{ds} \\ \frac{\partial Z}{\partial x_\rho} &= \sqrt{\frac{g_{\sigma\sigma} P_\sigma}{-g_{\rho\rho} P_\rho^2}} \frac{\partial A_\sigma}{\partial x_\rho} = \frac{dx_\sigma}{ds} \frac{\partial A_\sigma}{\partial x_\rho} = \frac{dp_\rho}{ds} \end{aligned} \quad (61)$$

The equations of motion are again of the form (59) with the required generalization to take account of the varying rest-mass.

Now since

$$\begin{aligned} m^2 &= E^2 - \Sigma P_r^2 \\ \frac{m}{E} \frac{dm}{ds} &= \frac{dE}{ds} - \Sigma \frac{dx_r}{dt} \frac{dP_r}{ds} \\ \frac{dm}{dt} &= -F_{4\sigma} \frac{dx_\sigma}{ds} - F_{r\sigma} \frac{dx_r}{dt} \frac{dx_\sigma}{ds} \end{aligned}$$

Thus

$$\frac{dm}{ds} = -F_{\mu\nu} \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} \quad (62)$$

$$\text{or, since } Z = -m, \quad \frac{dZ}{ds} = F_{\mu\nu} \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} \quad (63)$$

This invariant is the relativistic analogue of Rayleigh's dissipation function, a quadratic function of the velocities, the coefficients being functions of the co-ordinates and the time only. If we denote this function by  $R$ , the equations of motion may be written in the form

$$\frac{dP_\rho}{ds} = \frac{\partial R}{\partial \left( \frac{dx_\rho}{ds} \right)}, \quad P_\rho = g_{\rho\rho} m \frac{dx_\rho}{ds} \quad (64)$$

analogous to the non-relativistic equations.

From (55) and (63) we have

$$\frac{dZ}{ds} = 2 \frac{dA_\mu}{ds} \frac{dx_\mu}{ds} \quad (65)$$

and we note in passing that the condition for constant rest-mass is that the second member of (63) or (65) should vanish. We may use this result to deduce the fourth equation of (54) or (56) from (58) and (59), for

$$\begin{aligned} \frac{dY}{dt} &= \frac{\partial Y}{\partial x_r} \frac{dx_r}{dt} + \frac{\partial Y}{\partial p_r} \frac{dp_r}{dt} + \frac{\partial Y}{\partial t} = 2 \frac{dx_r}{dt} \frac{dp_r}{dt} + \frac{\partial Y}{\partial p_r} \frac{\partial A_r}{\partial t} + \frac{\partial A_4}{\partial t} \\ &= 2 \left( \frac{ds}{dt} \right)^2 \frac{dx_r}{ds} \frac{dp_r}{ds} + \frac{dx_r}{dt} \frac{\partial A_r}{\partial t} + \frac{\partial A_4}{\partial t} \\ \therefore \frac{dY}{ds} &= 2 \frac{ds}{dt} \left[ \frac{\partial A_\sigma}{\partial x_r} \frac{dx_\sigma}{ds} \frac{dx_r}{ds} \right] + \frac{dx_r}{ds} \frac{\partial A_r}{\partial t} + \frac{\partial A_4}{\partial t} \frac{dt}{ds} \\ &= 2 \frac{ds}{dt} \left( - \frac{\partial A_\sigma}{\partial t} \frac{dx_\sigma}{ds} \frac{dt}{ds} \right) + \frac{dx_r}{ds} \frac{\partial A_r}{\partial t} + \frac{\partial A_4}{\partial t} \frac{dt}{ds} = - \frac{\partial A_\sigma}{\partial t} \frac{dx_\sigma}{ds} \end{aligned}$$

But

$$Y = E + A_4$$

hence

$$\frac{dE}{ds} = \frac{dY}{ds} - \frac{\partial A_4}{\partial x_\sigma} \frac{dx_\sigma}{ds} = -F_{4\sigma} \frac{dx_\sigma}{ds}$$

which is the required result.

A striking property of the anti-Hamiltonian systems (59) or (61) is the substitution of anti-commuting brackets for the Poisson brackets of classical theory. Let  $f, g$  be functions of  $x_r$  and  $p_r$  and let

$$\{f, g\} = \sum_r \left[ \frac{\partial f}{\partial x_r} \frac{\partial g}{\partial p_r} + \frac{\partial f}{\partial p_r} \frac{\partial g}{\partial x_r} \right] \quad (66)$$

then

$$\{f, Y\} = \sum_r \left[ \frac{\partial f}{\partial x_r} \frac{dx_r}{dt} + \frac{\partial f}{\partial p_r} \frac{dp_r}{dt} \right] = \frac{df}{dt} \quad (67)$$

also

$$\{f, p_r\} = \frac{\partial f}{\partial x_r} \quad \{f, x_r\} = \frac{\partial f}{\partial p_r} \quad (68)$$

A constant of the motion therefore "anti-commutes" with  $Y$ . Corresponding results for  $f(p_\rho, x_\rho)$  with the function  $Z$  substituted for  $Y$  and the variable  $s$  for  $t$  are obvious:

$$\{f, Z\} = \frac{df}{ds} \quad \{f, p_\rho\} = \frac{\partial f}{\partial x_\rho} \quad \{f, x_\rho\} = \frac{\partial f}{\partial p_\rho} \quad (69)$$

It is of interest to note that in both Hamiltonian and anti-Hamiltonian systems defined by the function  $Y$  of (58), the expressions  $\{\dot{x}_i, \dot{x}_j\}$  vanish if the field  $F_{\mu\nu} = A_{\mu\nu} + A_{\nu\mu}$  vanishes.

The connection between the  $\{ \}$  bracket expressions (66) and the equations of motion (61) is not analogous to that between the Poisson expressions and

the Hamiltonian equations: for, let  $p_\rho, x_\rho \rightarrow P_\rho, X_\rho$  respectively, then if  $Z$  is invariant on transformation, clearly

$$\begin{aligned}\frac{dP_\mu}{ds} &= \frac{\partial Z}{\partial P_\nu} \{P_\mu, P_\nu\} + \frac{\partial Z}{\partial X_\nu} \{P_\mu, X_\nu\} \\ \frac{dX_\mu}{ds} &= \frac{\partial Z}{\partial P_\nu} \{X_\mu, P_\nu\} + \frac{\partial Z}{\partial X_\nu} \{X_\mu, X_\nu\}\end{aligned}\quad (70)$$

and the equations of motion are transformed covariantly only if

$$\{P_\mu, P_\nu\} = 0 = \{X_\mu, X_\nu\} \quad \text{and} \quad \{P_\mu, X_\nu\} = \delta_\nu^\mu \quad (71)$$

which conditions are analogous to the Poisson bracket conditions for the covariant transformation of the Hamiltonian equations. But of course since  $Z$  is to be invariant on transformation, the motion itself does not constitute such a transformation unless there is excluded from consideration the general case in which  $Z$  is not a constant of the motion. It may be shown by considering the infinitesimal transformations conforming with (71), that only if  $Z$  is linear in the  $p_\mu$  and the  $x_\mu$  will Equations (71) include the motion as an allowed transformation.\* This special case is not essentially anti-Hamiltonian since the equations of motion could be derived from a Hamiltonian function. Of course the form of (61) can be preserved if  $Z$  is allowed to transform covariantly, then, however, the physical significance of  $Z$  will be lost on transformation. Thus the anti-Hamiltonian system does not show the far-reaching properties that the Hamiltonian does with respect to transformation theory.

The equations of motion (61) can be handled by a different and more fruitful method which could be applied to certain dissipative systems in ordinary dynamics and which serves for the treatment of motion in a field specified by the tensor (of type iii)

$$\begin{aligned}F_{\mu\nu} &= \left( \frac{\partial A_\mu}{\partial x_\nu} - \frac{\partial A_\nu}{\partial x_\mu} \right) + \left( \frac{\partial B_\mu}{\partial x_\nu} + \frac{\partial B_\nu}{\partial x_\mu} \right) \\ &= A_{\mu\nu} + B_{\mu\nu}\end{aligned}\quad (72)$$

$A_{\mu\nu}$  being thus an antisymmetric and  $B_{\mu\nu}$  a symmetric tensor. With the equations of motion

$$\frac{dP_\mu}{ds} = F_{\mu\nu} \frac{dx_\nu}{ds} \quad P_\mu = m g_{\mu\nu} \frac{dx_\nu}{ds} \quad (73)$$

we have

$$-\frac{dm}{ds} = \frac{dx_\mu}{ds} \frac{dP_\mu}{ds} = B_{\mu\nu} \frac{dx_\mu}{ds} \frac{dx_\nu}{ds} \quad (74)$$

with the usual summation convention. Let us write

$$p_\mu = P_\mu - A_\mu \quad H = -\sqrt{-g_{\rho\rho} P_\rho^2}$$

then the equations of motion become

$$\frac{dp_\mu}{ds} = -\frac{\partial H}{\partial x_\mu} + B_{\mu\nu} \frac{dx_\nu}{ds} \quad \frac{dx_\mu}{ds} = \frac{\partial H}{\partial p_\mu} \quad (75)$$

\* See note in Appendix.

Now introduce the symbol

$$B[f, g] = \left( \frac{\partial B_r}{\partial x_\mu} + \frac{\partial B_\mu}{\partial x_r} \right) \frac{\partial f}{\partial p_\mu} \frac{\partial g}{\partial p_r} = B_{\mu r} \frac{\partial f}{\partial p_\mu} \frac{\partial g}{\partial p_r} = B[g, f] \quad (76)$$

and (75) may be written

$$\frac{dp_\mu}{ds} = - \frac{\partial H}{\partial x_\mu} + B[p_\mu, H] \quad \frac{dx_\mu}{ds} = \frac{\partial H}{\partial p_\mu} \quad (77)$$

The Poisson bracket

$$(f, H) = \frac{df}{ds} - B[f, H]$$

or

$$\frac{df}{ds} = (f, H) + B[f, H] \quad (78)$$

and

$$\frac{dH}{ds} = B[H, H] \quad (79)$$

while

$$(f, p_\mu) = \frac{\partial f}{\partial x_\mu} \quad (f, x_\mu) = \frac{\partial f}{\partial p_\mu} \quad (80)$$

Hence

$$\begin{aligned} B[f, g] &= \frac{\partial f}{\partial p_\sigma} (B_\sigma, g) + \frac{\partial g}{\partial p_\sigma} (B_\sigma, f) \\ &= (x_\sigma, f)(B_\sigma, g) + (x_\sigma, g)(B_\sigma, f) \end{aligned} \quad (81)$$

and of course

$$B[f, x_\mu] = 0$$

Now consider the transformation  $x_\mu, p_\mu \rightarrow X_\mu, P_\mu$  leaving  $H(p_\mu, x_\mu)$  invariant.

$$\begin{aligned} \frac{dP_\mu}{ds} &= (P_\mu, H) + B[P_\mu, H] \\ &= (P_\mu, H) + (x_\sigma, P_\mu)(B_\sigma, H) + (x_\sigma, H)(B_\sigma, P_\mu) \end{aligned} \quad (82)$$

$$(P_\mu, H) = \frac{\partial H}{\partial P_r} (P_\mu, P_r) + \frac{\partial H}{\partial X_r} (P_\mu, X_r), \quad (x_\sigma, P_\mu) = \frac{\partial P_\mu}{\partial p_\sigma},$$

$$(x_\sigma, H) = \frac{\partial H}{\partial P_r} \frac{\partial P_r}{\partial p_\sigma} + \frac{\partial H}{\partial X_r} \frac{\partial X_r}{\partial p_\sigma}, \quad (B_\sigma, P_\mu) = \frac{\partial B_\sigma}{\partial x_\rho} \frac{\partial P_\mu}{\partial p_\rho},$$

$$(B_\sigma, H) = \frac{\partial B_\sigma}{\partial x_\rho} \left( \frac{\partial H}{\partial P_r} \frac{\partial P_r}{\partial p_\rho} + \frac{\partial H}{\partial X_r} \frac{\partial X_r}{\partial p_\rho} \right)$$

Hence

$$\frac{dP_\mu}{ds} = \frac{\partial H}{\partial P_r} \left( (P_\mu, P_r) + B[P_\mu, P_r] \right) + \frac{\partial H}{\partial X_r} \left( (P_\mu, X_r) + B[P_\mu, X_r] \right)$$

and

$$\frac{dX_\mu}{ds} = \frac{\partial H}{\partial P_r} \left( (X_\mu, P_r) + B[X_\mu, P_r] \right) + \frac{\partial H}{\partial X_r} \left( (X_\mu, X_r) + B[X_\mu, X_r] \right). \quad (83)$$

In order that the form of Equations (82) may be preserved, we must have

$$\begin{aligned} \text{(i)} \quad & (P_\mu, X_\nu) + B[P_\mu, X_\nu] = -\delta_\nu^\mu \\ \text{(ii)} \quad & (P_\mu, P_\nu) + B[P_\mu, P_\nu] = B_{\mu\nu}' \\ \text{(iii)} \quad & (X_\mu, P_\nu) + B[X_\mu, P_\nu] = \delta_\nu^\mu \\ \text{(iv)} \quad & (X_\mu, X_\nu) + B[X_\mu, X_\nu] = 0 \end{aligned} \quad (84)$$

where  $B_{\mu\nu}'$  is the symmetric field tensor in the transformed system; it must be a function of the  $X_\mu$ 's only. From (i) and (iii) above we have

$$\text{(v)} \quad (X_\mu, P_\nu) = \delta_\nu^\mu$$

and

$$\text{(vi)} \quad B[P_\mu, X_\nu] = 0.$$

Let us now consider possible infinitesimal transformations of this system:

$$X_\mu = x_\mu + \epsilon \xi_\mu, \quad P_\mu = p_\mu + \epsilon \varpi_\mu. \quad (85)$$

From (84) (v)

$$\frac{\partial \varpi_\mu}{\partial p_\nu} + \frac{\partial \xi_\nu}{\partial x_\mu} = 0 \quad (86)$$

From (vi)

$$B_{\mu\rho} \frac{\partial \xi_\nu}{\partial p_\rho} = 0 \quad (87)$$

From (iv)

$$\frac{\partial \xi_\nu}{\partial p_\mu} - \frac{\partial \xi_\mu}{\partial p_\nu} = 0 \quad (88)$$

From (ii)

$$B_{\mu\nu}' = B_{\mu\nu} + \epsilon \left( B_{\mu\rho} \frac{\partial \varpi_\nu}{\partial p_\rho} + B_{\sigma\nu} \frac{\partial \varpi_\mu}{\partial p_\sigma} \right) + \epsilon \left( \frac{\partial \varpi_\mu}{\partial x_\nu} - \frac{\partial \varpi_\nu}{\partial x_\mu} \right) \quad (89)$$

Equations (86) and (88) allow us to write

$$\xi_\mu = \frac{\partial U}{\partial p_\mu}, \quad \varpi_\mu = -\frac{\partial U}{\partial x_\mu} + g_\mu(x_\sigma) \quad (90)$$

where  $g_\mu(x_\sigma)$  is a function of the  $x$ 's only and  $U$  is a function of the  $x$ 's and  $p$ 's.

Now on account of the transformation of the configurational co-ordinates

$$\begin{aligned} (B_{\mu\nu}')_{\text{co-ord}} &= B_{\alpha\beta} \frac{\partial x_\alpha}{\partial X_\mu} \frac{\partial x_\beta}{\partial X_\nu} \\ &= B_{\mu\nu} - \epsilon \left( B_{\mu\beta} \frac{\partial \xi_\beta}{\partial x_\nu} + B_{\alpha\nu} \frac{\partial \xi_\alpha}{\partial x_\mu} \right) \\ \therefore (B_{\mu\nu}')_{\text{dyn}} &= (B_{\mu\nu}')_{\text{co-ord}} + \epsilon \left( \frac{\partial g_\mu}{\partial x_\nu} - \frac{\partial g_\nu}{\partial x_\mu} \right) \end{aligned} \quad (91)$$

Thus in addition to the change due to the co-ordinate transformation,  $B_{\mu\nu}$  is altered by the addition of an infinitesimal antisymmetric tensor.

In order that the equations of motion should transform covariantly we require

$$g_\mu(x_\sigma) = B'[P_\mu, U] = B[p_\mu, U] \text{ to the first order,}$$

i.e.,

$$g_\mu(x_\sigma) = B_{\mu\nu} \frac{\partial U}{\partial p_\nu} = B_{\mu\nu} \xi_\nu \quad (92)$$

This is consistent with (87) for

$$\frac{\partial}{\partial p_\alpha} (B_{\mu\nu} \xi_\nu) = 0 \text{ (all } \alpha) \text{ and } B_{\mu\nu} \frac{\partial \xi_\nu}{\partial p_\alpha} = B_{\mu\nu} \frac{\partial^2 U}{\partial p_\nu \partial p_\alpha} = B_{\mu\nu} \frac{\partial \xi_\alpha}{\partial p_\nu}.$$

Equations (92) show us that  $\frac{\partial U}{\partial p_r}$  is a function of the  $x$ 's only; hence  $U$  is linear in the  $p$ 's. Thus the equations of motion can in this case be reduced to the form  $\frac{dx_\sigma}{ds} = f_\sigma$ ,  $\frac{dm}{ds} = g$ , where  $f_\sigma$  and  $g$  are functions of the  $x$ 's only: that is, we have to deal with motion in a field of velocity and rate of change of rest-mass. Apart from this special case it is clear that the transformations by which one passes from one trajectory to another are of different form from those by which one passes along a given trajectory following the motion. One is impressed therefore by the singular role played by Hamiltonian functions which are linear in the momenta.

### §5. Some Properties of the Fields

For convenience we shall refer to the antisymmetric tensor derived from the vector  $A_\mu$  as the  $E$ -field with potential  $A_\mu$ ; the corresponding field given by the symmetric tensor derived from  $A_\mu$  we shall refer to as the  $S$ -field.

(i) The additive superposition of corresponding  $S$ - and  $E$ -fields

$$G_{\mu\nu} = (A_{\mu\nu} + A_{\nu\mu}) + (A_{\mu\nu} - A_{\nu\mu}) = 2A_{\mu\nu}$$

is a field of potential momentum; for if

$$\begin{aligned} \frac{dP_\mu}{ds} &= G_{\mu\nu} \frac{dx_\nu}{ds} \\ \frac{d(P - 2A_\mu)}{ds} &= 0 \quad \text{i.e., } P - 2A_\mu = \text{constant.} \end{aligned} \quad (93)$$

(ii) In the special case where  $A_\mu = \frac{1}{2} \frac{\partial \varphi}{\partial x_\mu}$ ,  $\varphi$  being a function of the  $x$ 's, the  $E$ -field vanishes but not the  $S$ -field which is given by

$$F_{\mu\nu} = \frac{\partial^2 \varphi}{\partial x_\mu \partial x_\nu} \quad (94)$$

This is evidently a special case of (i) with  $-\frac{\partial \varphi}{\partial x_\mu}$  as the  $\mu$ -component of potential momentum. The system of motions defined by the function  $\varphi$  is of the same order of generality as the system of motions defined by a family of solutions of the Hamilton-Jacobi equation for a system of particle motions: this follows from the presence of a variable "constant" in (93).

(iii) We now consider some simple types of  $S$ -field in order to investigate the motion of a particle in them.

(a) Let  $A_1 = A_2 = A_3 = \text{constant}$ , then the equations of motion are

$$\frac{dP_r}{dt} = \frac{\partial A_4}{\partial x_r} \quad (r = 1, 2, 3)$$

hence this field could be described by the ordinary methods of dynamics,  $-A_4$  being the potential energy.



(b) Let  $A_2 = A_3 = A_4 = \text{constant}$ . The equations of motion are

$$\frac{d}{dt}(P_1 - A_1) = \frac{\partial A_1}{\partial x_1} \frac{dx_1}{dt}, \quad \frac{dP_2}{dt} = \frac{\partial A_1}{\partial x_2} \frac{dx_1}{dt}, \quad \frac{dP_3}{dt} = \frac{\partial A_1}{\partial x_3} \frac{dx_1}{dt}, \quad \frac{dP_4}{dt} = \frac{\partial A_1}{\partial t} \frac{dx_1}{dt}$$

hence if we change to  $x_1$  as the independent variable, this system is equivalent to (a) with potential momentum substituted for potential energy.

(c) Let  $\frac{\partial A_1}{\partial x_2} + \frac{\partial A_2}{\partial x_1} = F$  be the only non-zero component of the  $S$ -tensor, and let  $F$  be a constant. Then

$$\frac{dP_1}{dt} = F \frac{dx_2}{dt}, \quad \frac{dP_2}{dt} = F \frac{dx_1}{dt}, \quad \frac{dP_3}{dt} = 0, \quad \frac{dP_4}{dt} = 0 \quad (95)$$

hence

$$P_1 = Fx_2 + mv_1$$

$$P_2 = Fx_1 + mv_2$$

where  $mv_1$  and  $mv_2$  are constants. In the classical approximation of constant relative mass

$$\left. \begin{aligned} \frac{dx_1}{dt} &= \frac{F}{m} x_2 + v_1, & \frac{dx_2}{dt} &= \frac{F}{m} x_1 + v_2 \\ x_1 &= -\frac{mv_2}{F} + A \cosh \frac{Ft}{m} + B \sinh \frac{Ft}{m} \\ x_2 &= -\frac{mv_1}{F} + A \sinh \frac{Ft}{m} + B \cosh \frac{Ft}{m} \end{aligned} \right\} \quad (96)$$

where  $A$  and  $B$  are constants of integration. In the course of time  $x_1$  and  $x_2$  tend either to  $-\frac{mv_2}{F}$  and  $-\frac{mv_1}{F}$  respectively (when  $A + B = 0$ ) or to infinity (when  $A + B \neq 0$ ). The field  $F$  corresponds to a uniform magnetic field and the mean lifetime  $m/F$  corresponds to the period of Larmor precession.

(d) In a field with diagonal components only, suppose  $F_{11} = F_{22} = F_{33} = -b$  (a constant), then

$$\frac{dP_r}{dt} = -b \frac{dx_r}{dt} \quad (r = 1, 2, 3) \text{ or } P_r = bx_r + a_r$$

and in non-relativistic approximation

$$x_r = B_r \exp(-bt/m) + \text{constant} \quad (97)$$

Thus we may sum up by saying that constant negative diagonal components lead to exponentially damped motion. Constant components in the fourth column of the tensor matrix lead to accelerations due to constant forces. The remaining components correspond in their effects to a magnetic field acting on a charged particle, but with hyperbolic functions of the time substituted for circular ones.

(iv) If we are to regard Equations (47) for the continuous transformation of a meson into an electron as analogous to the equations of motion of an electron experiencing radiation damping according to a scheme such as that proposed by Dirac (1), then the field acting on the meson is of the same nature as the neutrino field produced by the meson and by which it loses energy

momentum and rest-mass. For it will be recalled that in Dirac's work the forces dissipating (or inversely stimulating) the electron's motion and corresponding to classical radiation damping forces are formally equivalent to an electromagnetic field the components of which depend in a simple way on  $\frac{dx_\mu}{ds}$ ,  $\frac{d^2x_\mu}{ds^2}$ , and  $\frac{d^3x_\mu}{ds^3}$ . We are led therefore to propose the idea that the neutrino field of a meson corresponds to the tensor defined by Equations (47). This tensor is neither symmetric nor antisymmetric, but may be obtained by adding an  $E$ -tensor and an  $S$ -tensor; let us call it an  $N$ -tensor. It must be proportional to the  $N$ -charge ( $n$ ) of the meson, just as the corresponding  $E$ -tensor would be proportional to the  $E$ -charge of the particle influenced by the corresponding field.

Let  $F_{\mu\nu} = n f_{\mu\nu}$  and in accordance with (47) choose the positive sign of  $N$ -charge so that

$$f_{\mu\nu} = \begin{array}{cccc} N & 0 & 0 & -M_z \\ & 0 & N & -M_y \\ \begin{array}{c} \nu \\ \rightarrow \\ \mu \downarrow \end{array} & 0 & 0 & N \\ & M_z & M_y & M_x & -N \end{array} \quad (98)$$

and define the charge and current density by

$$j^\mu = f^{\mu\nu} \quad (99)$$

i.e.,

$$\mathbf{j} = \text{grad } N - \dot{\mathbf{M}}$$

$$\rho = -\frac{\partial N}{\partial t} + \text{div } \mathbf{M}$$

Hence

$$\text{div } \mathbf{j} + \frac{\partial \rho}{\partial t} = \square N \quad (100)$$

Thus the  $N$ -charge is conserved only if  $N$  satisfies d'Alembert's equation. It is clear also that in the absence of distributed charge and current,  $N$  and the components of  $\dot{\mathbf{M}}$  satisfy d'Alembert's equation.

Now from the point of view of special relativity the tensor composed of the non-diagonal components of  $f_{\mu\nu}$  and with vanishing diagonal components is equivalent to an electromagnetic tensor with non-vanishing magnetic components as well as electrical ones. It seems then a natural step to identify  $N$ -charge with electric charge and consequently to propose as the new equations defining electric charge and current density

$$\begin{aligned} \mathbf{j} &= \text{grad } N + \nabla \times \mathbf{H} - \dot{\mathbf{E}} = \mathbf{j}_L + \text{grad } N \\ \rho &= -\dot{N} + \text{div } \mathbf{E} = \rho_L - \dot{N} \end{aligned} \quad (101)$$

where  $\mathbf{j}_L \rho_L$  are the electric current and charge density according to the Maxwell-Lorentz equations. (The factor  $4\pi$  has been omitted for simplicity.) In the special fields of (47),  $N$  would have then to be  $\sqrt{E^2 - H^2}$  or some function of  $E^2 - H^2$  and  $\mathbf{E} \cdot \mathbf{H}$  which reduces to  $|\mathbf{E}|$  when  $H = 0$ ; but in general this need not be so, for we can imagine an ordinary electromagnetic field superposed on the special field.

On the substitution of (101) for (99) Equation (100) still holds; it informs us that the scalar  $N$  appears in the field only as the result of the *creation or destruction of electricity*, and would be present neither in an electrostatic nor a galvanostatic field.

The new terms in Equations (101) alter the usual expressions of electromagnetic theory for the force per unit volume of distributed electricity as follows:

The spatial components by the addition of

$$\text{grad } (\tfrac{1}{2}N^2) + \nabla \times (NH) - \frac{\partial}{\partial t} (NE)$$

and the temporal component by  $\text{div } (NE) + \frac{\partial}{\partial t} (\tfrac{1}{2}N^2)$ .

Hence to the ordinary expression for the energy density in the medium must be added  $\tfrac{1}{2}N^2$  and to the Poynting flux  $NE$ . An electric charge which becomes the source of  $N$ -components could therefore emit energy and momentum in virtue of its electrostatic field without any electromagnetic radiation of optical type. On the other hand, for a field in which the diagonal components ( $N$ ) do not vanish, we have from (53)

$$N = \frac{dm}{ds}$$

where  $m$  is the rest-mass of a particle acted on by the field; hence its equations of motion may be written

$$m \frac{d^2 x_\mu}{ds^2} = E_{\mu\nu} \frac{dx_\nu}{ds},$$

$E_{\mu\nu}$  being the tensor derived from  $F_{\mu\nu}$  by equating its diagonal components to zero. Thus when  $E_{\mu\nu} = 0$ ,  $d^2 x_\mu/ds^2 = 0$ , and the velocity of the particle is unaffected by the field; the momentum does however suffer change on account of the change in rest-mass produced by the  $N$ -components of the field. The continuous actions with which we have dealt cannot be expected to represent the facts, if, as seems probable, the rest-mass of elementary particles is not continuously variable. Just as the classical theory of radiation has to be applied statistically in calculations of the effect of light on an atom, so the field we have been considering will have to be described as determining the probability of a change in the rest-masses of particles influenced by it, and the physical reality of neutrino radiation be established through the discovery of the transformation of electrons into mesons.

### Conclusion

In the discussion of fields based on investigation of potential momentum and the definition of dynamical systems by means of momentum fields, our interest has been primarily the exploration of new paths in dynamics. Certain interesting possibilities follow from the study of the meson-electron transformation and an attempt has been made to formulate a continuous representation of neutrino fields. Here the association of field components which cause change in the rest-mass of a particle under the action of the field, and the idea that the creation or destruction of electricity is the source of these components, may be a fruitful conception. It was not intended however, to develop these ideas in the present work nor to attempt to approach any of

the difficult problems connected with the forces between nuclear particles which are coupled with the theories of the meson and neutrino, and in the treatment of which the developments within the logical apparatus of quantum mechanics have become entangled with new conceptions which do not belong exclusively to quantum theory.

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### Appendix

In studying the transformation of the equation system (59) let us introduce the anti-Hamiltonian function

$$H(p_1, p_2, \dots, p_n, p_{n+1}, x_1, \dots, x_{n+1}) \\ = p_{n+1} - \frac{1}{2}z(s) + Z(p_1, \dots, p_n, x_1, \dots, x_n)$$

with the equations of motion

$$\frac{dp_r}{ds} = \frac{\partial H}{\partial x_r} \quad \frac{dx_r}{ds} = \frac{\partial H}{\partial p_r} \quad (r = 1, 2, \dots, n+1)$$

Then

$$\frac{dx_i}{ds} = \frac{\partial H}{\partial p_i} = \frac{\partial Z}{\partial p_i}, \quad \frac{dp_i}{ds} = \frac{\partial H}{\partial x_i} = \frac{\partial Z}{\partial x_i} \quad (i = 1, 2, \dots, n)$$

but

$$\frac{dp_{n+1}}{ds} = \frac{\partial H}{\partial x_{n+1}} \quad \frac{dx_{n+1}}{ds} = \frac{\partial H}{\partial p_{n+1}} = 1$$

therefore  $x_{n+1} = s$  and

$$\frac{dp_{n+1}}{ds} = \frac{\partial H}{\partial s} = -\frac{1}{2}\frac{dz}{ds}(s)$$

Hence  $H$  is invariant provided that  $z(s) = Z(p_1, \dots, p_n, x_1, \dots, x_n)$  following the motion. The conditions for the covariant transformation  $p_r \rightarrow P_r, x_r \rightarrow X_r$  of the equations of motion with  $H$  invariant are easily seen to be

$$\{P_r, P_s\} = 0 = \{X_r, X_s\} \quad \{P_r, X_s\} = \delta_{rs} \quad (r, s = 1, 2, \dots, n+1)$$

for

$$\frac{dP_r}{ds} = \{P_r, H\} = \{P_r, P_s\} \frac{\partial H}{\partial P_s} + \{P_r, X_s\} \frac{\partial H}{\partial X_s}.$$

In the case of the infinitesimal transformation

$$X_r = x_r + \epsilon \xi_r \quad P_r = p_r + \epsilon \varpi_r$$

we require

$$(i) \quad \frac{\partial \varpi_r}{\partial x_s} + \frac{\partial \varpi_s}{\partial x_r} = 0$$

$$(ii) \quad \frac{\partial \xi_r}{\partial p_s} + \frac{\partial \xi_s}{\partial p_r} = 0$$

$$(iii) \quad \frac{\partial \varpi_r}{\partial p_s} + \frac{\partial \xi_s}{\partial x_r} = 0$$

Hence if  $u, v = 1, 2, \dots, n$

$$\frac{\partial \varpi_u}{\partial x_v} + \frac{\partial \varpi_v}{\partial x_u} = 0, \quad \frac{\partial \xi_u}{\partial p_v} + \frac{\partial \xi_v}{\partial p_u} = 0, \quad \frac{\partial \varpi_v}{\partial p_u} + \frac{\partial \xi_u}{\partial x_v} = 0.$$

But if  $x_{n+1} = X_{n+1} = s$  and therefore  $\xi_{n+1} = 0$

$$\frac{\partial \varpi_{n+1}}{\partial x_u} + \frac{\partial \varpi_u}{\partial s} = 0, \quad \frac{\partial \varpi_{n+1}}{\partial s} = 0, \quad \frac{\partial \xi_u}{\partial p_{n+1}} = 0, \quad \frac{\partial \varpi_u}{\partial p_{n+1}} = 0,$$

and

$$\frac{\partial \varpi_{n+1}}{\partial p_u} + \frac{\partial \xi_u}{\partial s} = 0.$$

Since

$$\frac{\partial \varpi_u}{\partial x_u} = 0, \quad \varpi_u = \frac{\partial \varpi_{n+1}}{\partial x_u} s + f_u(x_v, p_v) \quad (v \neq u)$$

which leads with

$$\frac{\partial \varpi_u}{\partial x_v} + \frac{\partial \varpi_v}{\partial x_u} = 0$$

to

$$\frac{\partial^2 \varpi_{n+1}}{\partial x_u \partial x_v} = 0 \quad \text{and} \quad \frac{\partial^2 \varpi_{n+1}}{\partial p_u \partial p_v} = 0.$$

Thus  $\varpi_{n+1}$  does not depend on  $s$  explicitly and at most is linear in  $x_u$  and  $p_u$ . Now in the infinitesimal transformation corresponding to motion along a trajectory

$$\begin{aligned} \varpi_{n+1} &= \frac{dp_{n+1}}{ds} = \frac{\partial H}{\partial s} = -\frac{1}{2} \frac{dz(s)}{ds} = -\frac{1}{2} \frac{dZ}{ds} \\ &= -\frac{1}{2} \sum_u \left( \frac{\partial Z}{\partial x_u} \frac{dx_u}{ds} + \frac{\partial Z}{\partial p_u} \frac{dp_u}{ds} \right) = -\sum_u \frac{\partial Z}{\partial x_u} \frac{\partial Z}{\partial p_u}, \end{aligned}$$

hence in order that the motion may transform the equations of motion covariantly and leave  $H$  invariant we must have  $Z$  a linear function of  $x$  and  $p$ .



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## THE KINETICS OF THE THERMAL DECOMPOSITIONS OF THE LOWER PARAFFINS

### V. THE NITRIC OXIDE INHIBITED DECOMPOSITION OF *n*-BUTANE<sup>1</sup>

By E. W. R. STEACIE<sup>2</sup> AND H. O. FOLKINS<sup>3</sup>

#### Abstract

A detailed investigation of the inhibition by nitric oxide of the thermal decomposition of *n*-butane has been carried out over the temperature range 500° to 550° C.

In all cases it was found that inhibition decreased with increasing butane concentration. This suggests that radical recombination occurs in the normal decomposition by ternary collisions with butane molecules acting as third bodies.

The activation energies of the normal and inhibited reactions have been determined. For high pressures the two values are in good agreement, viz., 58,200 and 57,200 cal. per mole respectively. The products of the inhibited reaction were also found to be the same as those of the normal reaction.

It is concluded that free radical processes predominate, involving comparatively short chains.

#### Introduction

The effect of nitric oxide on the ethylene oxide sensitized decomposition of *n*-butane has recently been studied in this laboratory (6). It was found that nitric oxide was not completely efficient as a chain-breaker, and the experiments suggested that the normal decomposition proceeds by comparatively short free radical chains. The present paper is a continuation of this work, and deals with the inhibition by nitric oxide of the normal thermal decomposition of *n*-butane.

Hobbs and Hinshelwood (2, 3) have found that the inhibition of several hydrocarbon decompositions by nitric oxide is dependent upon the initial pressure of the hydrocarbon involved. In all cases they noted that inhibition diminished as the partial pressure of the hydrocarbon was increased.

Echols and Pease (1) investigated the inhibition of the *n*-butane decomposition. They reported maximum inhibition at a partial pressure of nitric oxide in the neighbourhood of 20 mm.

The activation energy of the over-all reaction in the *n*-butane decomposition is in the neighbourhood of 59 Kcal. (5, 7). Rice and Johnston (4)

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estimate 65.4 Kcal. for the split into free radicals. This is only slightly above the value for the normal decomposition, and suggests a primary rupture of the butane molecule into radicals, followed by short chains. With the object of throwing further light on the nature of the chain processes, experiments have been performed to determine the relative magnitude of the activation energies of the normal and of the inhibited reactions. The products of the reactions have also been compared.

### Experimental

The static method was used, and the reaction was followed by observing the rate of change of pressure and by analysis. The apparatus and procedure were similar to those of a previous investigation (7). The reaction vessel was of fused quartz, and had a capacity of 750 cc.

The partial pressures of both butane and nitric oxide were varied over a wide range, and the rates of reaction were compared with those obtained at the same butane pressure in the absence of nitric oxide.

Analyses of the products of the reaction were made by low-temperature distillation in a still of the Podbielniak type. Where necessary several runs were made under identical conditions in order to accumulate sufficient products for analysis.

*n*-Butane was obtained in cylinders from the Ohio Chemical and Mfg. Co. The cylinder gas contained 99% of *n*-butane, and was fractionally distilled before use. Nitric oxide was prepared by the nitrometer method.

### Results

#### *A. Maximum Inhibition and the Effect of Pressure*

A series of runs was made at 525° C. with initial pressures of butane varying from 4 to 60 cm., and of nitric oxide from 0.5 to 6 cm. As previously observed, it was found that the greatest inhibitory effect occurred during the early stages of the decomposition. Initial rates of decomposition are therefore the most reliable criterion of inhibition. These initial rates can be obtained with considerable accuracy, since the pressure-increase-time curves approximate straight lines in the early stages of the inhibited reaction. This is illustrated by Fig. 1 and by the velocity constants given in Table I.

The results for the series of runs at 525° C. are summarized graphically in Fig. 2, in which the initial rates (mm. per min.) are plotted against the concentration of nitric oxide. The different curves represent different partial pressures of butane. The initial rates were determined by taking the tangent to the rate curve at the origin for each individual experiment. Inspection shows that maximum inhibition is attained when the concentration of nitric oxide is between 1 and 2 cm. There is a gradual diminution of inhibition as the pressure of the substrate is increased. A summary of the initial rates and the resulting "apparent" chain lengths is given in Table II.



TABLE I  
DATA FOR TYPICAL RUNS AT 525° C.

Normal decomposition			Inhibited decomposition	
Initial butane press, 40.0 cm.			Butane, 40.10 cm.; NO, 2.00 cm.	
Time, min.	$\Delta p$ , cm.	$k \times 10^6$ , sec. <sup>-1</sup>	$\Delta p$ , cm.	$k \times 10^6$ , sec. <sup>-1</sup>
0	0.00	—	0.00	—
1	1.04	44.1	0.26	10.7
2	1.84	39.4	0.58	12.1
3	2.40	34.5	0.90	12.5
4	3.02	32.7	1.24	13.0
5	3.54	31.0	1.60	13.5
6	4.08	30.0	1.96	13.9
7	4.64	29.4	2.28	14.0
8	5.04	28.1	2.66	14.3
10	5.95	26.8	3.40	14.7
12	6.70	25.5	4.10	15.0
14	7.34	24.2	4.76	15.1
16	8.12	23.6	5.42	15.1
18	8.80	23.0	6.14	15.4
20	9.45	22.4	6.86	15.6
22	10.05	21.8	7.52	15.7
24	10.65	21.5	8.25	16.0
26	11.12	20.9	8.74	15.8
28	11.60	20.4	9.40	15.9
30	12.14	20.1	10.22	16.0
35	13.38	19.4	11.62	16.3
40	14.75	19.1	13.12	16.5
50	17.05	18.5	16.16	17.2
60	19.14	18.0	18.54	17.1

TABLE II  
NITRIC OXIDE INHIBITED REACTION AT 525° C.

Butane press., mm.	Initial rates (mm./min.) for different butane pressures					
	80 mm.	160 mm.	200 mm.	320 mm.	400 mm.	600 mm.
NO, 0.00 mm.	2.1	4.1	7.0	10.5	13.0	25.0
NO, 5.0 mm.	0.35	0.70	1.20	3.0	4.0	8.0
Normal rate	6.0	5.9	5.8	3.5	3.3	3.1
Inhib. rate						
NO, 10 mm.	0.32	0.60	1.10	2.10	3.10	7.0
Normal rate	6.4	6.8	6.3	5.0	4.2	3.6
Inhib. rate						
NO, 20 mm.	0.25	0.60	0.90	1.80	3.0	5.7
Normal rate	8.4	6.8	6.6	5.8	4.3	4.3
Inhib. rate						
NO, 40 mm.	0.40	0.70	—	2.10	3.60	7.8
Normal rate	5.2	5.9	—	5.0	3.6	3.2
Inhib. rate						
NO, 60 mm.	—	1.00	1.40	3.20	4.20	7.5
Normal rate	—	4.1	5.0	3.3	3.1	3.3
Inhib. rate						

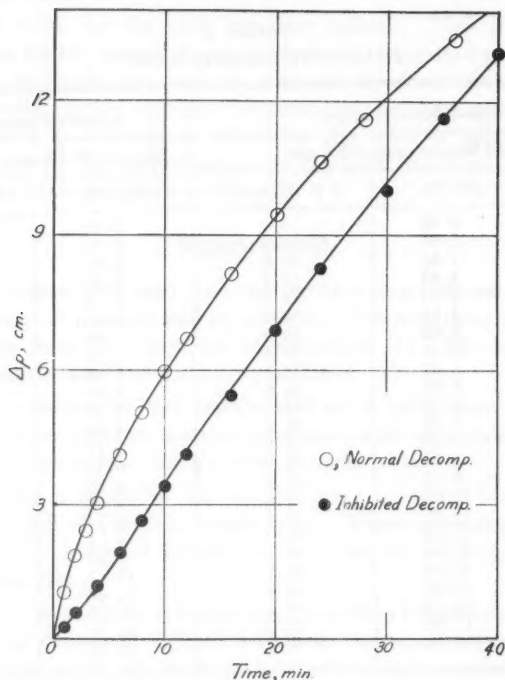


FIG. 1. Pressure-increase-time curves for typical runs at 525° C. Initial butane pressure, 40 cm.

The effect of butane pressure is quite evident. Thus for 20 mm. of nitric oxide the mean chain length varies from 8.4 for 80 mm. of butane to 4.3 for a butane pressure of 600 mm. These chain lengths are based on the relative initial rates of corresponding uninhibited and inhibited reactions. If it is as assumed on the basis of (6) that nitric oxide is not completely efficient as a chain breaker, the true chain length, in each case, will be somewhat greater than the value assigned here.

Inspection of a similar graph of  $T_{25}$  plotted against concentration of nitric oxide affords similar results, although they are not as trustworthy since inhibition has become quite small at this stage of the reaction.

The slight increase of the inhibited rate at high concentrations of nitric oxide, as shown in Fig. 2, is perhaps due to a slight amount of oxidation, but it is very small in relation to the inhibition attained.

#### B. The Effect of Temperature on Inhibition

The effect of temperature on inhibition was next investigated. The results of a series of experiments at 550° C. are given in Table III and Fig. 3, and those of a series at 500° C. in Table IV and Fig. 4.

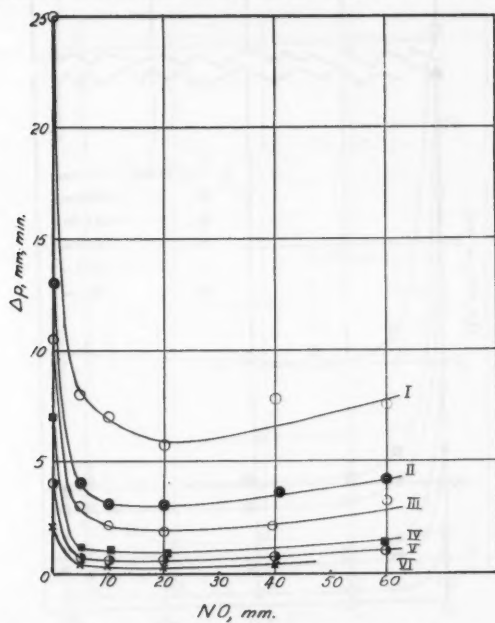


FIG. 2. Influence of butane pressure and concentration of nitric oxide on inhibition. Initial rates plotted against NO concentration.

Curve	I	II	III	IV	V	VI
Butane press., cm.	60	40	32	20	16	8

TABLE III  
NITRIC OXIDE INHIBITED REACTION AT 550° C.

Butane press., mm.	Initial rates (mm./min.) for different butane pressures					
	80 mm.	160 mm.	200 mm.	320 mm.	400 mm.	600 mm.
NO, 0.0 mm.	5.9	12.6	18.0	34.0	44.0	76.0
NO, 5 mm.	1.0	3.7	5.3	10.0	12.5	22.5
Normal rate	5.9	3.4	3.4	3.4	3.5	3.3
Inhib. rate						
NO, 10 mm.	1.1	3.6	4.3	8.7	10.5	20.0
Normal rate	5.4	3.5	4.2	4.1	4.2	3.8
Inhib. rate						
NO, 20 mm.	1.2	3.3	3.5	8.3	10.6	20.7
Normal rate	5.0	3.8	5.0	4.1	4.1	3.6
Inhib. rate						
NO, 40 mm.	0.9	3.3	3.9	8.2	9.6	21.2
Normal rate	6.5	3.8	4.5	4.0	4.5	3.5
Inhib. rate						

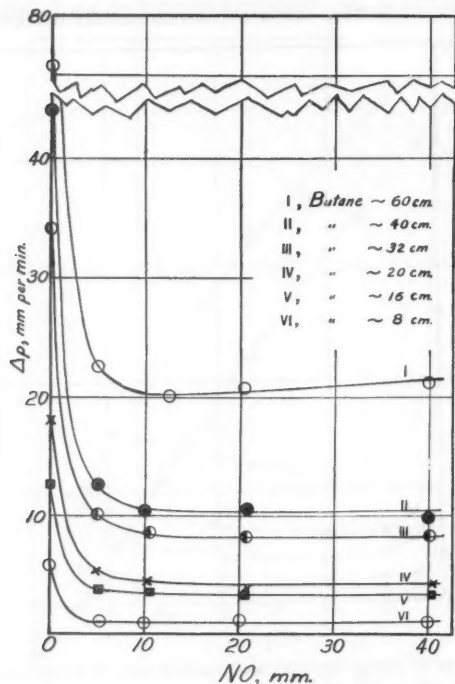


FIG. 3. Influence of butane pressure and nitric oxide concentration on inhibition at 550° C. Initial rates plotted against NO concentration.

TABLE IV  
 NITRIC OXIDE INHIBITED REACTION AT 500° C.

Butane press., mm.	Initial rates (mm./min.) for different butane pressures			
	80 mm.	160 mm.	320 mm.	600 mm.
NO, 0.0 mm.	0.6	1.5	3.5	7.5
NO, 5 mm.	0.03	0.10	0.49	1.80
Normal rate	20.0	15.0	7.1	4.2
Inhib. rate				
NO, 10 mm.	0.03	0.09	0.38	1.50
Normal rate	20.0	16.6	9.2	5.0
Inhib. rate				
NO, 20 mm.	0.03	0.10	0.45	1.60
Normal rate	20.0	15.0	7.7	4.7
Inhib. rate				
NO, 40 mm.	—	0.15	0.50	1.70
Normal rate	—	10.0	7.0	4.5
Inhib. rate				

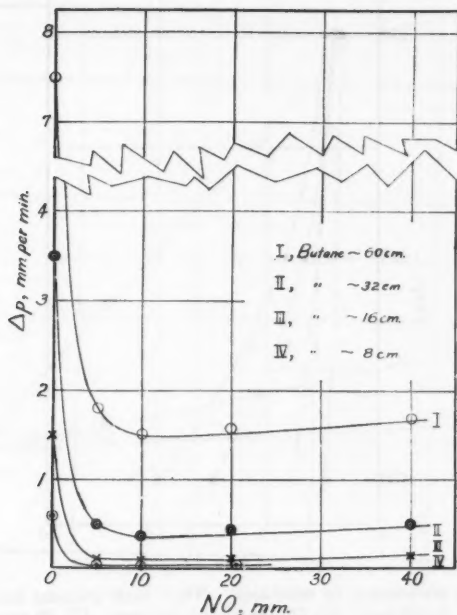


FIG. 4. Influence of butane pressure and nitric oxide concentration on inhibition at 500° C. Initial rates plotted against NO concentration.

It is apparent that temperature has considerable influence on the degree of inhibition over the range investigated. The effect is shown in Fig. 5, in which temperature is plotted against the apparent chain length obtained by inhibiting with 20 mm. partial pressure of nitric oxide.

It will be noted that at high butane pressures the apparent chain length is almost independent of temperature, while at low pressures it decreases rapidly with increasing temperature. It follows that the temperature coefficient of the inhibited reaction will be much higher at low pressures than at high. The activation energy of the reaction can, of course, be calculated only from initial high pressure rates. The value has been arrived at by calculating the apparent activation energies at various partial pressures of butane, and extrapolating the results to infinite pressure. For the maximum inhibited reaction, the mean values of the apparent activation energy at various partial pressures of butane are:—

Initial butane pressure, cm.	60	32	16	8
Apparent activation energy, Kcal.	64.0	71.1	85.2	93.9

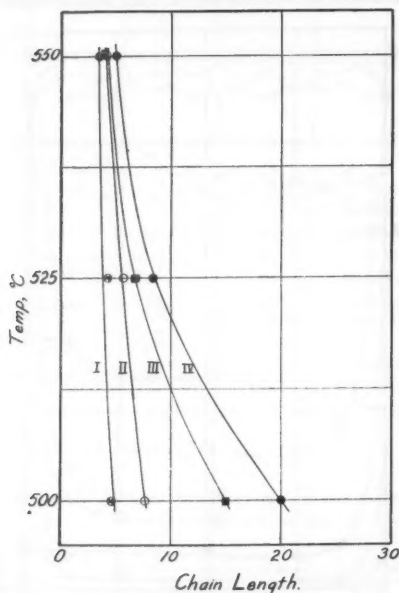


FIG. 5. Effect of temperature on inhibition. Nitric oxide pressure constant at 20 mm. Butane pressures: I, 600 mm.; II, 320 mm.; III, 160 mm.; IV, 80 mm.

The extrapolations to infinite pressure of these values, and of corresponding values for the normal reaction, are shown in Fig. 6. The values obtained are:—

Inhibited reaction	57.2 Kcal.
Normal reaction	
(from initial rates)	58.4
(from $T_{25}$ )	58.0
(found by Steacie and Puddington (7) )	58.7

It may therefore be concluded that, within the experimental error, the activation energies of the normal reaction and of the maximum inhibited reaction are identical.

### C. The Products of the Reaction

The products of the normal decomposition have already been investigated over a wide range of pressure, temperature and extent of reaction by Steacie and Puddington (7). In the present work the only object in analyses was to compare the products of the inhibited reaction with those of the normal decomposition.

The samples were withdrawn from the reaction vessel at  $T_{25}$  by expansion into a two litre bulb through a small liquid air trap. Two or three experiments under identical conditions were necessary in order to obtain sufficient products for analysis. The sample was transferred by means of a Toepler pump to a

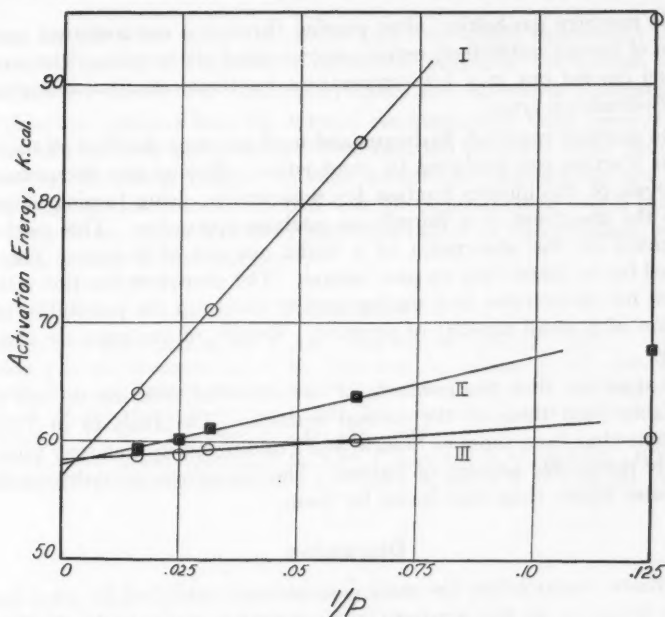


FIG. 6. Extrapolation of activation energies to infinite pressure.

I. Inhibited decomposition.

II. Normal decomposition, calculated from  $T_{25}$ .

III. Normal decomposition, calculated from initial rates.

TABLE V  
ANALYSES AT  $T_{25}$  FOR RUNS AT 525° C.

Products, mole per cent							Per cent undecom- posed $C_4H_{10}$
$H_2$	$CH_4$	$C_2H_4$	$C_2H_6$	$C_3H_8$	$C_4H_8$	$C_4H_6$	
Inhibited reaction: butane 40 cm., NO 2 cm.							
7.6	28.7	13.7	15.1	28.1	6.7	—	71.0
Inhibited reaction: butane 60 cm., NO 2 cm.							
6.7	29.9	13.8	14.4	27.1	8.1	—	73.4
Normal decomposition: butane 60 cm.							
7.1	25.3	14.1	14.4	29.6	9.2	—	74.1

portable mercury gas-holder, after passing through a concentrated aqueous solution of ferrous sulphate to remove unconsumed nitric oxide. The analysis was then carried out in a low-temperature fractional distillation apparatus of the Podbielniak type.

In the analyses reported, hydrogen and methane were distilled off together, and this fraction was analyzed by combustion. Butene was determined by an analysis of the butane fraction for unsaturates, using fuming sulphuric acid as the absorbent in a Burrell gas analysis apparatus. This method is complicated by the absorption of a slight amount of butane. This was corrected for by blank runs on pure butane. The propylene fraction was also analyzed for unsaturates in a similar way to check up the possibility of the formation of a small amount of propane. Results of analyses are given in Table V.

It is apparent that the products of the inhibited reaction do not differ appreciably from those of the normal reaction. The analyses in Table V differ somewhat from those of Steacie and Puddington in that they found no definitely detectable amount of butene. The percentage of hydrogen found here is also higher than that found by them.

### Discussion

The above results follow the same general trend exhibited by other hydrocarbons in so far as the apparent chain length is concerned. Unlike the ethane decomposition, however, the activation energy of the maximum inhibited reaction does not differ appreciably from that of the normal decomposition.

The fact that the inhibitory effect of nitric oxide decreases as the pressure of butane increases suggests that chain termination, caused by the combination of free radicals and nitric oxide, is in competition with a chain breaking mechanism of the normal decomposition which is dependent upon the butane concentration. It would thus appear that chains are being broken, in the majority of cases, by recombination of free radicals with butane molecules acting as third bodies.

The fact that the products of the inhibited reaction are not appreciably different from those of the normal reaction, together with the identity of the activation energies, throws considerable light on the nature of the chain process. If there were a few very long chains, accompanied by considerable decomposition through direct molecular rearrangement, then complete suppression of the chains should leave only the molecular decomposition. It seems exceedingly unlikely, however, that both mechanisms should lead to identical products, since it would be necessary to have three separate molecular splits



combined in exactly the right proportions to duplicate the products of the chain reaction.



If we assume a few very long chains, and incomplete suppression by nitric oxide, the difficulty still remains, since partial inhibition would mean a change in the relative amounts of reaction by chain and non-chain processes.

It therefore appears that the normal decomposition must involve a large number of relatively short chains. The addition of nitric oxide then merely diminishes the chain length, without completely suppressing the chains. Under these circumstances, provided that the residual chain length is appreciable, there is no reason to expect much alteration in the products or in the activation energy of the reaction.

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## THE FRACTIONATION OF TURNER VALLEY CRUDE OILS USING STEDMAN COLUMNS<sup>1</sup>

By R. M. DONALD<sup>2</sup>

### Abstract

A sample of Turner Valley crude oil was distilled using a fractionating column 5 ft. high, and it is shown that a number of the compounds present may be isolated in high concentration.

At temperatures much above 100° C. the separations are naturally not as complete, but, judging by the absorption spectra of the higher boiling fractions, each compound is still concentrated in a very narrow boiling range.

A very large number of the possible aliphatic and naphthenic compounds are shown to be present, and it is also shown that the aromatic content of the oil is extremely complex.

The purpose of this investigation was to fractionate a sample of the new crude oil of the Turner Valley field, Alberta, in a very efficient fractionating column in order to identify as many compounds in the crude oil as time and apparatus would permit. The proportion of each compound in the crude oil was estimated when possible.

### *Examination of Sterling Pacific No. 3 Crude Oil, Royalite Oil Company*

The general properties of the crude oil are as follows:—

A.P.I. gravity at 60° F.	= 45.8
Specific gravity at 60° F.	= 0.7964
Colour	= Light green.

### *Viscosity*

Temperature, ° F.	Saybolt viscosity
13.8	41.1
32.0	36.4
60.0	32.5

A Hempel distillation was run on the crude, and the results are given in Table I.

On the basis of the United States Bureau of Mines' method of classification, this crude oil would be classed "intermediate" base but favouring the "paraffinic" rather than the "naphthenic".

### Physical Examination of Hempel Samples

A portion of each Hempel sample 3 to 8 was treated with twice its volume of 98% sulphuric acid for 15 min. at 30° C. The acid was drawn off and the sample was given two more similar treatments. It was washed with water and then with a 10% solution of sodium hydroxide, and finally dried over

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TABLE I  
DISTILLATION OF STERLING PACIFIC CRUDE OIL

Temperature range, °C.	Volume percentage distilled	Sample No.	Density, $d_4^{20}$	Refractive index, $n_D^{20}$	Aniline point	Average boiling point, °C.
<i>Hempel distillation</i>						
21- 50	3.3	1	0.635	1.36400	—	42.0
50- 75	5.3	2	.6745	1.38181	58.5	66.0
75-100	9.4	3	.7197	1.40304	49.2	89.5
100-125	11.3	4	.746	1.41815	45.2	112.5
125-150	10.7	5	.766	1.43170	42.8	113.5
150-175	8.0	6	.779	1.43863	46.5	162.0
175-200	6.0	7	.790	1.44236	56.3	187.0
200-225	6.3	8	.8023	1.44877	62.7	212.0
225-250	7.3	9	.8236	1.45961	—	238.0
250-275	6.0	10	.8363	1.46684	—	263.0

*Vacuum distillation; absolute press., 40 mm. Hg. I.B.P., 161° C.*

161-175	0.7	11	0.8555	1.47276	—	287.0
175-200	4.0	12	.8603	1.47873	—	313.0
200-225	4.7					
225-250	4.0	13	.871	1.48586	—	338.0
250-275	3.3	14†	.8685	1.48304	—	363.5
275-300	3.0	15				
Residue	5.7					
Loss	1.0					

†Refractive index and density of sample No. 14 were determined after removing wax.

calcium chloride. The refractive index, density, and the aniline point of each fraction were redetermined. These data are given in Table II.

The aniline point reported here is the critical solution temperature of equal parts by volume of the sample and aniline. The aniline used gave a value of 70° C. with pure *n*-heptane. This purity was suggested as being desirable by Brame and Hunter (1).

TABLE II  
DATA ON ACID TREATED SAMPLES

Sample No.	Density, $d_4^{20}$	Refractive index, $n_D^{20}$	Aniline point, °C.
3	0.7193	1.40276	50.7
4	.7346	1.41084	54.4
5	.7409	1.41281	67.6
6	.7559	1.42039	70.6
7	.7223	1.42879	72.6
8	.7884	1.43741	74.0

From the above data, several methods are available for estimating the proportions of paraffins, naphthenes and aromatics in the samples, and a comparison was made of the results obtained by the graphical method of Kurtz and Headington (6) and by means of the curves given by Tizard and Marshall (9) for the estimation of aromatic compounds in such samples. By the latter method the aromatics are determined by the change in aniline point caused by extraction of the samples with sulphuric acid; and comparison of the aniline point of the extracted sample with a plot of the boiling point vs. aniline point of the known paraffin and naphthene compounds gives the composition of this extracted residue.

The compositions of the fractions estimated by means of the two methods are given in Table III.

TABLE III  
ESTIMATED COMPOSITION OF HEMPEL SAMPLES

Sample No.	Kurtz and Headington method			Tizard and Marshall method		
	Paraffins	Naphthenes	Aromatics	Paraffins	Naphthenes	Aromatics
1	100.0	—	—	—	—	—
2	78.3	21.7	—	83.0	17.0	—
3	43.2	54.8	2.0	44.2	53.9	1.9
4	43.0	46.2	10.8	30.7	58.3	11.0
5	57.9	17.5	24.5	47.5	23.4	29.1
6	52.1	22.2	25.7	52.2	19.3	28.5
7	38.0	42.9	19.1	41.4	39.2	19.4
8	41.9	44.7	13.4	39.4	47.3	13.3

The compositions of only the first eight fractions were estimated, as the graphical method has been tested up to 200° C. only.

These first eight fractions represent 61.5% of the crude oil. Therefore, according to the estimates obtained by means of the Kurtz and Headington method, this portion of the crude oil contains 13.4% aromatics, 52.4% paraffins, and 34.2% naphthenes. It will be noted that the two methods do not give quite concordant results.

### Close Fractionation of Oil

After the above preliminary tests on small samples, 33.2 litres of the lyewashed crude oil was divided into fairly close cuts, using a gauze packed column [(8), Type No. 5] 3 in. in diameter and 2 ft. long, with a brass still head constructed as shown in Fig. 1. About 40% of the oil was distilled from the heavier residue in six roughly equal fractions. A reflux ratio of 10 : 1 was used at the start and this was gradually increased to about 20 : 1 at the end.

The fractions obtained in this way were then redistilled using a similar column 5 ft. high, provided with a glass still head as shown in Fig. 2. This head allows the reflux ratio to be set at any desired value. The column and

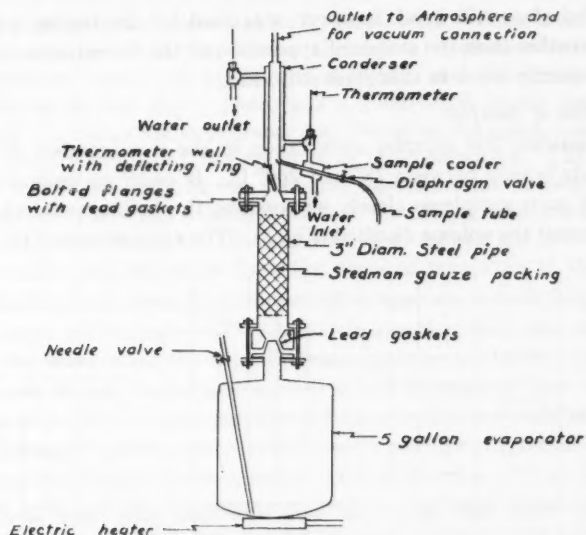


FIG. 1. Three-foot column with brass still head.

still head were wound with nichrome wire, the windings being connected in series and the spacing of turns being adjusted to provide a temperature gradient of about  $4^{\circ}\text{C.}$  per ft. and to maintain the still head at about  $25^{\circ}\text{C.}$  below the temperature of the top of the column. This margin was provided to ensure that the thermometer was never superheated, and below  $60^{\circ}\text{C.}$  the still head heating coil was not used. Still head temperatures were measured with a platinum resistance thermometer calibrated at the standard points;

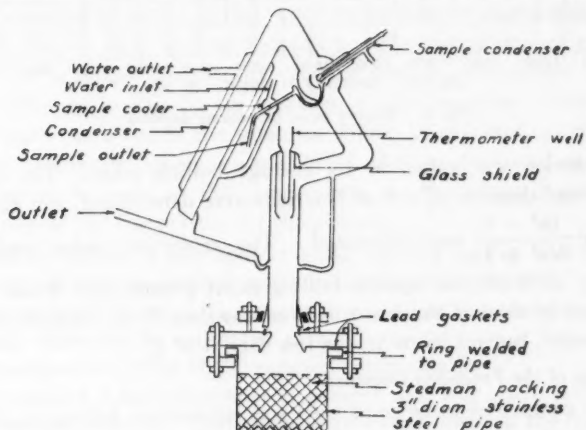


FIG. 2. Glass still head.

the shielded glass still head, however, was used for the boiling point determinations rather than the standard apparatus, as the thermometer is required to read correctly when in this glass still head.

#### *Examination of Samples*

Approximately 200 samples were taken in the fractionation of that part of the crude boiling between 28° and 200° C. In order to estimate the composition of each sample as closely as possible, the boiling point of each was plotted against the volume distilled (Fig. 3). The temperature of the midpoint

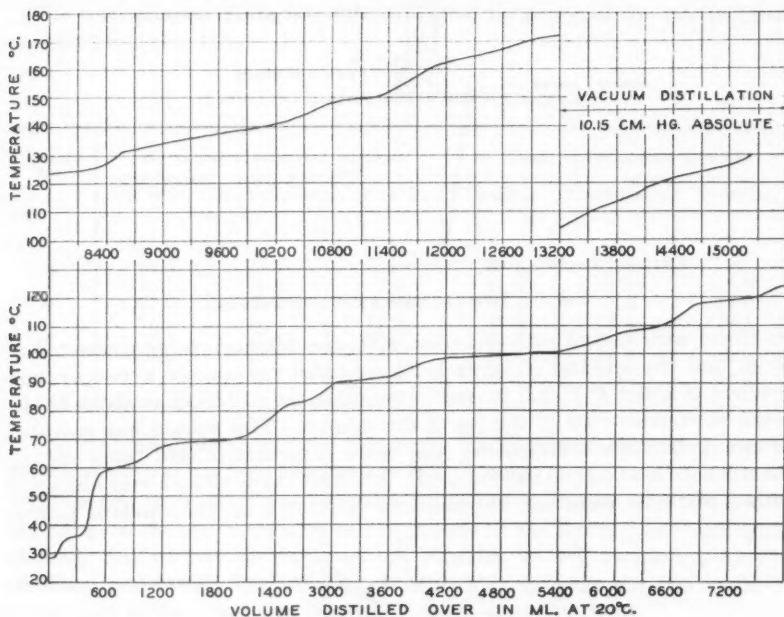


FIG. 3. Boiling point vs. volume distilled.

of each fraction was taken as its average boiling point. The refractive index,  $n_D^{20}$ , and density,  $d_4^{20}$ , of all fractions were determined, and the specific refractivity  $\frac{(n^2 - 1)}{d(n^2 + 2)}$  was calculated. The refractive index and specific refractivity were plotted against boiling point giving Figs. 4 and 5. The boiling range of most of the fractions was less than 1° C., that of a few was slightly greater, but for many it was less than 0.5° C.

#### *Composition of the Fractions Obtained*

The first compound to be condensed was isopentane, boiling at 28° C., as indicated by the boiling point curve. It should be noted that there was

considerable butane, and some lighter hydrocarbons. These were estimated by passing the lighter hydrocarbons through a condenser cooled with a freezing mixture, about 1% by volume of butane and lighter hydrocarbons being collected in this way. There was a good break in the boiling point curve at 28° C., indicating isopentane, and the refractive index measurements on these samples confirmed the presence of this compound. The refractive index was a little low but this was probably due to a small amount of butane in the samples. There was a definite break in the boiling point curve at 36° C. corresponding to *n*-pentane. The percentages of isopentane and *n*-pentane in each sample were estimated from the physical properties of the samples.

Fig. 4-B definitely shows that some cyclopentane was present but there was no break in the boiling point curve; this indicates that there was only a small amount. However, when the large difference between the boiling points of the compounds in this region is considered, it would be expected that nearly pure cyclopentane would be separated, but 2,2-dimethylbutane boils at about the same temperature, and thus there is obtained a mixture of 2,2-dimethylbutane and cyclopentane, which distil together. The proportion of these compounds present in each sample was estimated from its physical properties in conjunction with the triangle obtained by plotting the refractive index against boiling point of 2,2-dimethylbutane, cyclopentane, and *n*-pentane. Obviously in an estimation of this kind there is difficulty in knowing when one compound ceases to come over and another starts, but, if care is taken, such uncertainties can be reduced as far as is desired. In the case under consideration, *n*-pentane, cyclopentane, and 2,2-dimethylbutane are assumed to distil over from 36° to 50° C., until the curve representing sample composition crosses the side of the triangle representing cyclopentane and 2,2-dimethylbutane (about 50° C.). When this occurs it is assumed that the *n*-pentane has been completely removed and 2,3-dimethylbutane starts distilling over with cyclopentane and 2,2-dimethylbutane. The proportion of each can be estimated in a similar manner by plotting specific refractivity against refractive index (as in Fig. 6) and drawing similar triangles. This was done, and the results were much the same, as would be expected, as the methods are similar. However, there is a possibility that results based on the temperature may be in error, as the temperature in a transition region may not be indicative of the composition of the sample.

2,3-Dimethylbutane is indicated in small amount by Fig. 4-B and also by the slope of the volume distilled curve in passing through 60° C.

2-Methylpentane is certainly present in the oil in considerable quantities, and it may therefore be estimated rather accurately, as it was present in high concentration in most of the samples containing it.

The compound 3-methylpentane is present also but there is less of this than of 2-methylpentane. There is no appreciable break in the boiling point curve (Fig. 3) corresponding to 3-methylpentane. Benzene starts to distil



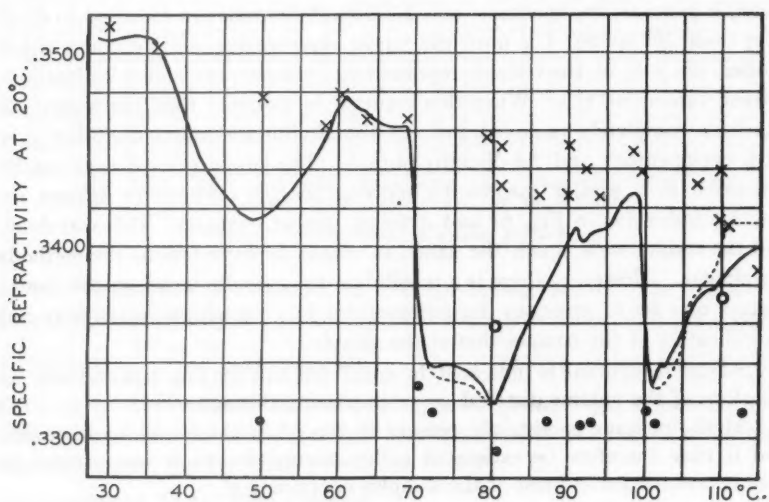
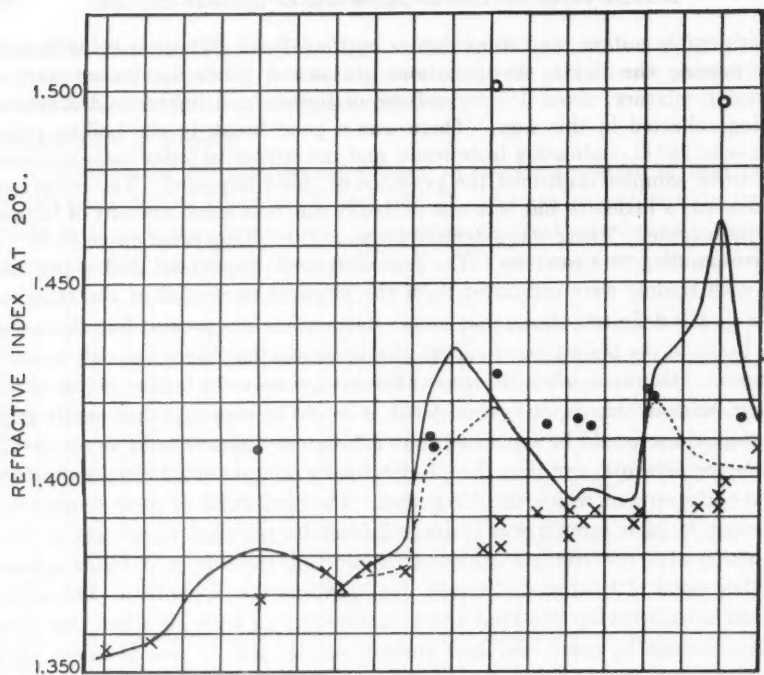


FIG. 4-A. Refractive index; 20° to 115° C.  
 FIG. 4-B. Specific refractivity; 20° to 115° C.

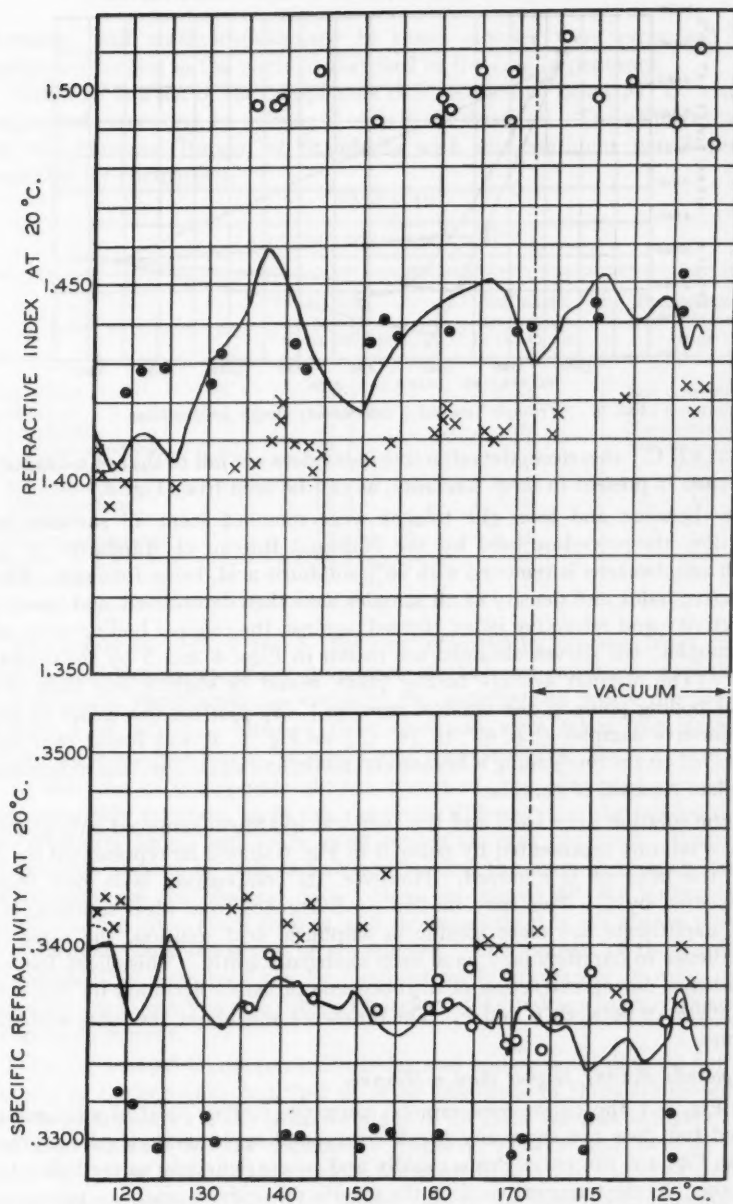


FIG. 5-A. Refractive index; 115° C. to end.

FIG. 5-B. Specific refractivity; 115°C. to end.

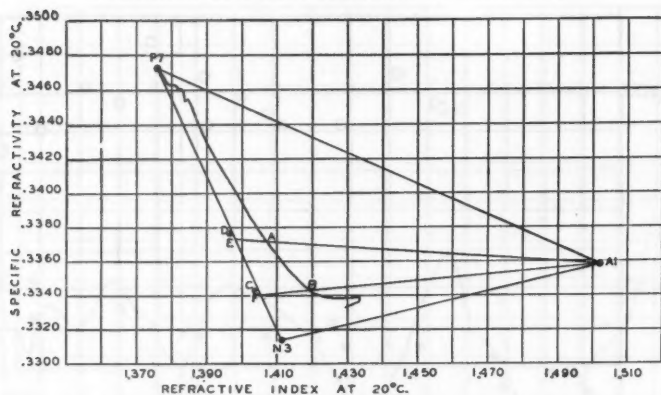


FIG. 6. "Triangle" method of determining sample compositions.

over at 62° C.; therefore, the refractive index does not fall to that of *n*-hexane. *n*-Hexane is present in large amounts, as can be seen from Fig. 3.

The benzene and later the toluene were removed from all samples by nitration, the procedure used by the National Bureau of Standards (3), in which nitrobenzene is removed with 96% sulphuric acid, being followed. The refractive index and density of all samples were then determined, and specific refractivity and refractive index plotted against the original boiling point of the samples; the curves obtained are shown in Figs. 4 and 5 by the dotted lines. (The original average boiling point would be slightly less than the actual boiling point of the residual samples.) By plotting the values of the benzene-free samples (b.p. 69° to 74° C.) on Fig. 6, it was found that the points fell on the line joining *n*-hexane and methylcyclopentane, this indicating complete removal of benzene.

If the solution were ideal and the chemical treatment removed only aromatics, a mixture represented by point *B* in Fig. 6 should be represented by *F* after the benzene is removed. However, its composition is in fact then represented by *C*. This may be due to divergence from ideal solution, or, since naphthenes are more soluble in sulphuric acid solution, the ratio of naphthenes to paraffins may have been changed slightly. This slight loss of naphthenes during extraction of nitrobenzene probably accounts for most of the difference between *C* and *F*. The difference was about the same with all samples.

#### *Compounds Boiling Higher than n-Hexane*

In Fig. 4-A the curve rises rapidly when the boiling point of *n*-hexane is passed but does not show any break corresponding to methylcyclopentane, but in Fig. 4-B the curve drops rapidly and points definitely to methylcyclopentane. As the temperature rises, the specific refractivity reaches a minimum at methylcyclopentane and then rises slightly before falling to another minimum corresponding to cyclohexane. The proportions of cyclohexane,

benzene, and methylcyclohexane in these samples were estimated from suitable triangles in the manner discussed in the case of pentanes.

Table IV is a list of the compounds detected boiling below 81° C. with the estimated percentage by volume of each in the crude oil. The values obtained by the National Bureau of Standards with mid-continent petroleum are included for comparison.

TABLE IV  
COMPOUNDS BOILING BELOW 81° C.

Compound	Boiling point, ° C. at 760 mm.	Estimated percentage in the crude	Percentage in mid-continent crude
Isopentane	28.0	0.38	Not determined
<i>n</i> -Pentane	36.0	.79	Not determined
Cyclopentane	49.5	.09	Not determined
2,2-Dimethylbutane	49.7	.11	Not determined
2,3-Dimethylbutane	58.1	.27	0.04
2-Methylpentane	60.2	.94	.09
3-Methylpentane	63.2	.56	.18
<i>n</i> -Hexane	68.7	2.40	.33
Methylcyclopentane	72.1	0.82	.20
Benzene	80.2	.32	.08
Cyclohexane	80.8	.76	.33

The points on Figs. 4 and 5 that are indicated by crosses, black circles, and open circles represent the properties of the pure paraffinic, naphthenic, and aromatic compounds respectively, the constants of which are listed in Tables A, B, and C. Most of these constants were taken from data tabulated by Ward and Kurtz (11) and Egloff and Grosse (4, 5).

In the case of compounds already discussed, the estimated percentages are reasonably accurate, as in this range the differences in the boiling points are relatively large, and fairly good separation was obtained. When the compounds present in each sample are known, the amount of each can be calculated from the physical data. However, above 80° the boiling point differences are often much smaller, and consequently it is not always possible to determine the composition of all samples. The amount of those present in considerable quantities can be obtained fairly accurately in most cases, but some uncertainty is still caused by lack of definite knowledge of the other compounds present.

From 80° to 100° C. the refractive index and boiling point data do not rule out any of the heptanes, but they do show that none of them are present in very large amounts. The refractive index of all these samples is higher than would be expected for the heptanes; Tongberg, Fenske, and Sweeney (10) found this to be true for all fractions obtained from about twenty gasolines in this boiling range. This is, no doubt, due to the dimethylcyclopentanes, which have boiling points from 87.5° to 93° C., and will distil over with the heptanes. As this mixture is so complex in this range it would be insepar-

able in the column used in this investigation. The boiling point curve indicates considerable quantities of material distilling at about 90.0° C. This is the boiling point of 2-methylhexane (*A*), a compound found in considerable quantities by Bruun and Hicks-Bruun (2).

2,3-Dimethylpentane (*B*) boils at about the same temperature but would not be expected in quantities nearly as large as those of 2-methylhexane, as it would probably be less stable. Since (*B*) was not found by the National Bureau of Standards it seems reasonable to assume for present purposes that the material boiling at 90.0° C. is largely 2-methylhexane. The boiling point curve also shows a compound at 92° C. and this no doubt is 3-methylhexane (*C*), which would be expected when (*A*) is present in large quantities. The proportion of (*C*) has not been reported by the National Bureau of Standards as this has not yet been determined. However, their preliminary estimates in other articles indicate that somewhat less is present than is reported for (*A*). *n*-Heptane is, of course, present in large amounts, as is shown by the boiling point and refractive index curves.

*Compounds Boiling above 100° C.*

The refractive index and boiling point indicate also considerable quantities of a naphthene at about 101° C. This has been generally reported as methylcyclohexane, but as ethylcyclopentane has nearly the same physical and chemical properties it would be very difficult to separate them. The National Bureau of Standards have reported only methylcyclohexane, although they suspected the presence of some ethylcyclopentane. From their data it is noted that the ratio of methylcyclohexane (*D*) to ethylcyclohexane (*E*) is 3 : 1, and it would be reasonable to suppose that the ratio of methylcyclopentane (*F*) to ethylcyclopentane (*G*) would be about the same. At this rate, since there is 0.82% of (*F*), we may expect 0.17% of (*G*). Accordingly, it does not seem reasonable to disregard the ethylcyclopentane.

Toluene is present in large amounts and begins to distil at 98° C. It was removed from each sample by nitration. The physical properties of the toluene-free samples are plotted in Figs. 4 and 5, and are indicated by dotted lines. The concentration of toluene in the samples remains approximately constant at about 6% from 98° to 100.5° C. The physical properties of the toluene-free samples in this range fell so close to the original curve that they are not included in Figs. 4 and 5. After a temperature of 100.5° C. is attained the concentration of toluene in the samples rises rapidly, reaching a maximum of 70% at its normal boiling point, 110° C. The properties of the samples before and after toluene removal were plotted on a diagram similar to Fig. 6, toluene, *n*-heptane, and methylcyclohexane forming the corners of the triangle. The results were similar to those given for benzene. The points representing the toluene-free oil fell nearly on the line joining *n*-heptane and methylcyclohexane but somewhat nearer the *n*-heptane corner than would be expected if the solutions were ideal.

The temperature rises rapidly from 110° to 117° C.; this indicates that very little of the branched octanes in this region are present. Leslie (7)

reports 0.5% or more of 2-methylheptane boiling at 117.2° C. In the present case, however, there was a distinct break in the boiling point and other properties at 118° C. 4-Methylheptane boils at 118° C. and 3-methylheptane at 119° C.; it is therefore very probable that all three methylheptanes account for the break at 118° C.

The dimethylcyclohexanes boil at 119° to 124° C. The refractive index indicated at least some, if not all, of these compounds. The National Bureau of Standards report an octanaphthene at 119.9° C., 1,3-dimethylcyclohexane at 120.3° C., and smaller amounts of 1,2-dimethylcyclohexane at 123.4° C. In the present work the boiling point and refractive index indicate considerable quantities of naphthene boiling at about 120° C., but there is no break at 123° C., so there is very little 1,2-dimethylcyclohexane. The properties of 1,1-, 1,3-, and 1,4-dimethylcyclohexanes, which all boil around 120° C., are very nearly the same and would be very difficult to separate.

Large amounts of *n*-octane boiling at 125.5° C. are present, as was shown by the boiling point and refractive index curves.

Ethylcyclohexane was definitely indicated at 131.8° C., as shown by the specific refractivity curve. Aromatics are present in all the fractions boiling between 127° and 142° C. These can be removed by nitration and thus estimated more accurately. Also, other compounds in this range might be detected when the properties of the samples free of aromatics are plotted. The aromatics are, no doubt, the three xylenes and some ethylbenzene. These could be separated and identified by a combination of physical and chemical methods, but such a separation is rather difficult and was not attempted in this investigation.

The specific refractivity curve seems to indicate naphthenes at about 137° C. This may be due to one or more of the trimethylcyclohexanes, as some of these boil in this range. This curve also has a small paraffinic peak at about 142.5° C. which is probably due to one or more of the methyloctanes. The curve also indicates naphthenes at about 147° C. Tongberg, Fenske, and Sweeney (10) report that a nonanaphthene occurs in most gasolines at this point. Some of the trimethylcyclohexanes boil in this range and may be responsible for this dip in the specific refractivity curve.

*n*-Nonane is present, boiling at about 150° C., as is shown by the boiling point and refractive index curves.

The specific refractivity curve indicates naphthenes boiling from 150° to 155° C. Naphthenes in this range have been detected by others (5), and are possibly propyl- and isopropylcyclohexanes, with many other possibilities.

The concentration of aromatics in all samples boiling between 148° and 170° C. was relatively high. The trimethylbenzenes boil in this range and very likely account for most of the aromatics in these fractions. Normal and isopropyl benzenes boil in the same range and are probably present in appreciable quantities. *Tert*-, *sec*-, and isobutylbenzenes also boil between these temperatures and are probably present. The dip in the specific refrac-



tivity curve between 165° and 170° C. seems to indicate naphthenes, which may be the *sec*- and *tert*-butylcyclohexanes.

Table V gives a preliminary estimate of the compounds so far detected boiling between 80° and 174° C. The values reported by the National Bureau of Standards on a mid-continent petroleum are included for comparison.

TABLE V  
COMPOUNDS BOILING BETWEEN 80° AND 174° C.

Compounds	Preliminary estimate per cent, by volume	Mid-continent petroleum
Dimethylcyclopentanes	0.75	0.4
2-Methylhexane	1.0	.3
3-Methylhexane	0.7	.2
<i>n</i> -Heptane	1.6	.9
Methylcyclohexane } Ethylcyclopentane }	2.2	.34
Toluene	2.0	.30
2-, 3-, and 4-Methylheptane	0.5	.7
Dimethylcyclohexanes	.8	.54
<i>n</i> -Octane	.95	1.0
Ethylcyclohexane	.6	0.1
Three xylenes } Ethylbenzene }	2.5	.31
<i>n</i> -Nonane	0.8	1.0
Trimethylbenzenes	1.6	0.28

At this point the still head was remodelled so that the oil could be fractionated at reduced pressure and the samples could be withdrawn without affecting the distillation.

The fraction of the crude oil normally boiling between 174° and 200° C. was fractionated in the same column at approximately 10 cm. of mercury, absolute pressure.

Decane is definitely indicated at 174° C., but, since all the samples in this range contained naphthenes and aromatics and there was no appreciable break in the boiling point curve at this point, it is impossible to estimate its proportion in the crude from the data obtained. Most of the decane was removed in the atmospheric distillation, but some was removed in the first part of the vacuum distillation. Judged from the refractive index of the samples, the separation was approximately the same in the two distillations.

All samples obtained in the fractionation of the portion normally boiling between 174° and 200° C. contained quite a high proportion of aromatic compounds. However, there was an "aromatic peak" in the refractive index curve at a temperature corresponding to about 183° C. at normal pressure. The samples obtained at this point contained about 30% of aromatics. The diethylbenzenes boil from 176.5° to 182.5° C., and very likely they account for most of the aromatics in the fractions boiling between 174° and 182° C.



There may also be some 1,2,3-trimethylbenzene in this range. However, the peak in the refractive index curve is too high to be accounted for by any of these compounds. *n*-Butylbenzene probably accounts for the aromatic peak at 183, although other aromatics are likely present. The tetramethylbenzenes boil between 193° and 204° C. and there is little doubt that these account for some of the aromatic compounds in the fractions boiling between 185° and 200° C. There is another aromatic peak at 193° C. which is possibly due to *tert*- and *sec*-amylbenzenes. The specific refractivity gives a slight indication of naphthenes at 177° C. There is a very definite "naphthenic valley" in the specific refractivity curve, corresponding to 181° C., which may be accounted for by *n*-butylcyclohexane and that at 177° C. may be due to *tert*- and *sec*-butylcyclohexane.

Both the refractive index and the specific refractivity indicate appreciable quantities of paraffins at about 189° C. This is probably due to one or more of the methyldecane. *n*-Undecane is definitely indicated at a temperature corresponding to about 195° C. For the reasons mentioned in the case of decane, its proportion in the crude oil could not be estimated from the data obtained.

#### Ultraviolet Absorption Spectra of Samples Containing Aromatics

From the results given above it is not feasible to decide which of the possible aromatic compounds are present in the oil distilling below 180° C., and, consequently, the absorption spectra of samples boiling from 129° to 177° C. were taken in the region of 2600 Å, using an end-on hydrogen discharge tube and a Hilger Model E Quartz spectrograph. A small amount of each sample was diluted with 1.5 cc. of highly purified *n*-heptane which itself showed no absorption bands, and successive additions of 0.05 cc. of this diluted material were made to a further 1.5 cc. of the *n*-heptane in a quartz cell 5 mm. thick on the spectrograph.

The spectra obtained are shown (as positives) in Fig. 7 in which the top band of each spectrum was taken with the lowest concentration, and the concentration increases linearly with each lower band. As the concentration of aromatic constituents and the strength of the absorption bands varied widely from sample to sample, the first dilution was made using amounts of sample from 0.03 to 0.6 cc. This volume used is given in the third column of the figure, and it might perhaps be noted that succeeding spectra are from serial samples except in a few cases, where a spectrum has been deleted as showing no appreciable change from the preceding.

It will be realized that in order to compare the quantities of the constituents in different samples it is necessary to allow for the different concentrations, thus, roughly speaking, the top band of the first spectrum relates quantitatively with the third band of the second spectrum, and it is therefore evident that the absorption bands shown in the first spectrum are rather weak.

At this time no real effort was made to identify all the spectra, as there is no doubt that many of the samples contained more than a single aromatic

compound, and in any case the absorption spectra are not available for many of the more complex compounds.

It is however evident that each of the xylenes is present, and that they distil considerably below their normal boiling points, but it is obvious that a very large number of other aromatic compounds are also present. Thus of the spectra from 5 to 21, only the groups—6 and 7; 10 and 11; 16, 17, and 18—show any appreciable similarity between succeeding spectra, although they are in many cases taken over very small temperature ranges. It might perhaps be noted that the wave-length scale is that provided in the instrument, and while not quite exact, as the spectra were taken with a constant setting, they are all strictly comparable.

In view of the evidently large number of compounds present, and the great variety of possibilities, including up to four or, possibly in some arrangements, even five aliphatic carbon atoms on the benzene nucleus, which might occur in this boiling range, it seemed a distinct problem in itself to consider their identification in any detail. It is, however, of interest to note (*a*) how rapidly the absorption spectrum varies with change of boiling point when the oil is fractionated with this equipment; (*b*) the relative completeness with which such compounds are evidently concentrated in very small cuts; and also (*c*) the large number of aromatic compounds present in this range of boiling point.

### Conclusions

By using only a 5 ft. column of this very efficient Stedman packing, most of the possible, and all of the probable, compounds boiling between 20° and 80° C. were detected, and the amount of each was estimated. Many compounds were separated with a purity better than 85% in one distillation. With longer columns, even better separation could be effected, and, by using large volumes of crude oil and redistilling, very pure compounds could be obtained by fractional distillation alone. Also, many compounds boiling above 80° C. could be separated in a fairly pure state.

Although it has been shown that as a rule aromatic compounds do not form constant boiling mixtures with paraffins and naphthenes, they distil below their normal boiling point. However, the aromatic compounds could be removed from the fractions of the first distillation by carefully controlled nitration. The residual oil, consisting mainly of paraffins and naphthenes, could be redistilled in a very efficient column and thus a better separation of paraffins and naphthenes obtained. This work shows that by increasing the effectiveness of the fractionating column, nearly all the compounds in the gasoline fractions at least could be detected and estimated with little treatment other than distillation.

It is evident that with these columns, or with others, similar but slightly more effective, the so-called "true boiling point curve" can be obtained, giving in considerable detail the composition of very complex mixtures.

# PLATE I

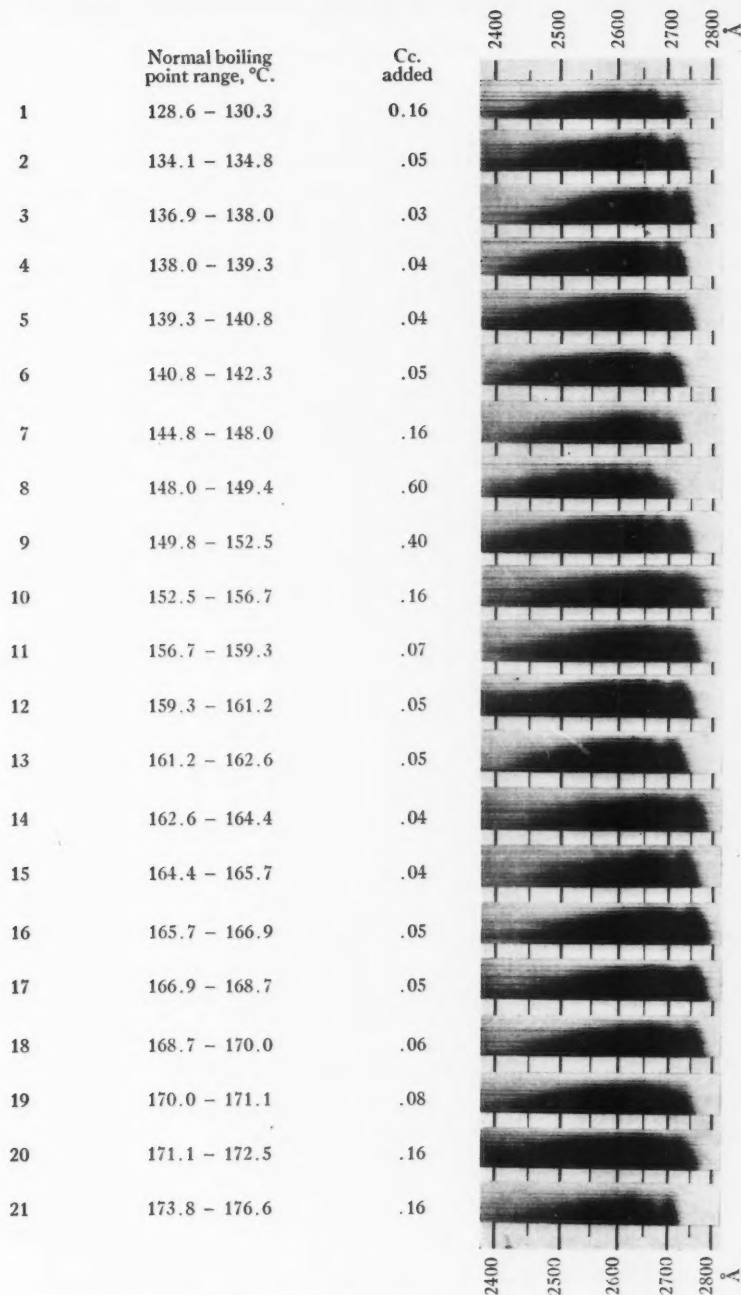
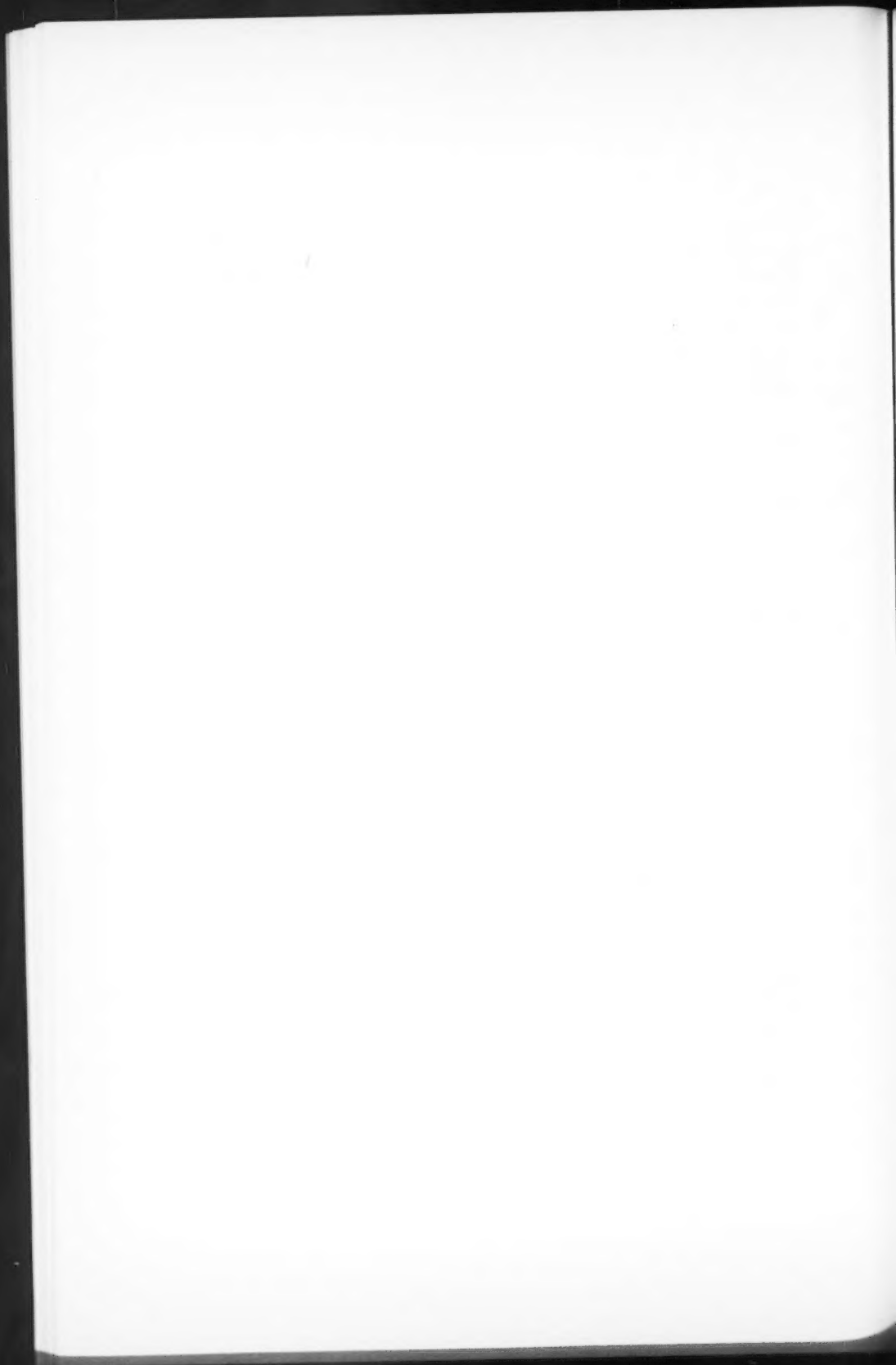


FIG. 7. Absorption spectra of samples boiling from 129° to 177° C.



## Properties of Hydrocarbons

TABLE A

## PARAFFINIC COMPOUNDS

Compound	B.p., ° C.	$d_4^{20}$	$n_D^{20}$	S. R.
Isopentane	30.0	0.62007	1.355	0.35146
<i>n</i> -Pentane	36.0	.62632	1.35769	.3503
2,2-Dimethylbutane	49.8	.6493	1.3692	.34768
2,3-Dimethylbutane	57.92	.6612	1.3750	.3462
2-Methylpentane	60.24	.6532	1.3718	.3477
3-Methylpentane	63.16	.6642	1.3775	.3467
<i>n</i> -Hexane	68.76	.6595	1.3752	.34726
2,2-Dimethylpentane	78.9	.6737	1.38233	.34569
2,4-Dimethylpentane	80.8	.6745	1.38233	.34528
2,2,3-Trimethylbutane	80.9	.6900	1.38940	.34308
3,3-Dimethylpentane	86.0	.6934	1.39114	.34277
2,3-Dimethylpentane	89.7	.6952	1.39201	.34263
2-Methylhexane	90.0	.6789	1.38509	.34527
3-Methylhexane	91.8	.6870	1.38873	.34404
3-Ethylpentane	93.3	.6952	1.39201	.34254
<i>n</i> -Heptane	98.4	.6836	1.38777	.34493
2,2,4-Trimethylpentane	99.3	.6918	1.3916	.34389
2,2-Dimethylhexane	106.9	.6953	1.3930	.34327
2,5-Dimethylhexane	109.4	.69378	1.39297	.34385
2,4-Dimethylhexane	109.8	.7030	1.3955	.3414
3,3-Dimethylhexane	111.3	.710	1.3955	.34109
2,3,3-Trimethylpentane	114.6	.7253	1.4072	.33878
2,3-Dimethylhexane	115.8	.7118	1.4015	.34174
2-Methylheptane	117.2	.6980	1.3936	.34238
3,4-Dimethylhexane	117.9	.7193	1.4044	.34029
4-Methylheptane	118.0	.7165	1.4035	.34098
3-Ethylhexane	118.6	.7128	1.4014	.34115
3-Methylheptane	119.0	.7054	1.3982	.34230
<i>n</i> -Octane	125.68	.70256	1.39758	.34326
2,4-Dimethylheptane	133.3	.7167	1.4036	.34226
2,6-Dimethylheptane	133.2	.7129	1.4025	.34194
2,5-Dimethylheptane	135.8	.7142	1.4042	.34258
3,3-Dimethylheptane	137.5	.7304	1.4095	.33885
4-Ethylheptane	138.5	.7407	1.41564	.33854
3,3-Diethylpentane	139.2	.75222	1.4197	.33623
2,3-Diethylpentane	140.6	.7235	1.4085	.34128
4-Methyloctane	142.2	.7243	1.4078	.34045
2-Methyloctane	143.2	.7134	1.4032	.34220
3-Methyloctane	144.2	.7210	1.4065	.34105
<i>n</i> -Nonane	150.72	.71780	1.40541	.34096
2,4-Dimethyloctane	153.1	.7244	1.4090	.3437
2,6-Dimethyloctane	159.0	.7288	1.4114	.3410
3,6-Dimethyloctane	160.0	.7364	1.4145	.3397
2,7-Dimethyloctane	160.25	.7254	1.4084	.3403
4- <i>n</i> -Propylheptane	161.7	.7360	1.414	.3395
5-Methylnonane	165.1	.73255	1.4122	.3431
4-Methylnonane	165.7	.73234	1.4123	.3400
2-Methylnonane	166.8	.72805	1.4099	.3402
3-Methylnonane	167.8	.73335	1.4125	.3396
<i>n</i> -Decane	174.02	.73014	1.41191	.3407
2,6-Dimethylnonane	175.0	.7439	1.4176	.3385
5-Ethylonane	184.0	.7507	1.4207	.3376
2,6-Dimethyldecane	195.0	.7572	1.4240	.3370
<i>n</i> -Undecane	195.84	.74025	1.41706	.3398
5- <i>n</i> -Propylnonane	196.6	.7543	1.4239	.3382

B.p., boiling point at 760 mm. Hg.; S.R., Lorentz-Lorenz specific refractivity.

TABLE B. NAPHTHENIC COMPOUNDS

Compound	B. p., ° C.	$d_4^{20}$	$n_D^{20}$	S.R.
Cyclopentane	49.5	0.7447	1.4075	0.3309
Ethylcyclobutane	70.5	.7284	1.4004	.3329
Methylcyclopentane	72.1	.7482	1.4103	.3314
Cyclohexane	80.8	.7785	1.4263	.3293
1,1-Dimethylcyclopentane	87.5	.7552	1.4139	.3308
1,3-Dimethylcyclopentane	91.5	.7563	1.4144	.3307
1,2-Dimethylcyclopentane	93.0	.7534	1.4126	.3309
Methylcyclohexane	100.4	.7695	1.4237	.3314
Ethylcyclopentane	101.8	.7654	1.4202	.3308
1,2,4-Trimethylcyclopentane	113.0	.7565	1.4156	.3314
Cycloheptane	119.0	.8099	1.4440	.3280
1,4-Dimethylcyclohexane ( <i>cis</i> )	119.0	.7638	1.4223	.3321
1,3-Dimethylcyclohexane ( <i>trans</i> )	119.4	.772	1.4254	.3315
1,4-Dimethylcyclohexane ( <i>trans</i> )	121.0	.7727	1.4253	.3324
1,3-Dimethylcyclohexane ( <i>cis</i> )	121.0	.7735	1.4269	.3318
1,2-Dimethylcyclohexane ( <i>trans</i> )	124.0	.7799	1.4273	.3294
1,2-Dimethylcyclohexane ( <i>cis</i> )	127.0	.7822	1.4303	.3302
<i>n</i> -Propylcyclopentane	130.0	.7718	1.4250	.3313
Ethylcyclohexane	131.8	.78804	1.43304	.3298
1,1,3-Trimethylcyclohexane	138.0	.7930	1.4367	.3302
1-Methyl-2-isopropylcyclopentane	142.5	.7792	1.4279	.3301
1,2,3-Trimethylcyclohexane ( <i>cis</i> )	146.0	.7930	1.4367	.3302
Cyclo-octane	149.0	.8347	1.4586	.3272
1,2-Diethylcyclopentane	149.2	.791	1.4343	.3294
1,1-Diethylcyclopentane	151.0	.8028	1.4388	.3275
1,2-Diethylcyclopentane	152.6	.805	1.4400	.3274
Isopropylcyclohexane	152.3	.799	1.4411	.3306
Propylcyclohexane	154.5	.793	1.4369	.3303
1,2,3,4-Tetramethylcyclohexane	161.0	.7934	1.4371	.3303
1-Methyl-3-isopropylcyclohexane	168.5	.7948	1.4380	.3292
<i>tert</i> -Butylcyclohexane	170.0	.811	1.4464	.3291
<i>sec</i> -Butylcyclohexane	171.5	.797	1.4391	.3300
Isoamylcyclopentane	171.0	.7868	1.4240	.3310
1,2-Methyl- <i>n</i> -propylcyclohexane	176.0	.808	1.4445	.3291
<i>sec</i> -Butylcyclohexane	179.0	.809	1.4458	.3295
<i>n</i> -Butylcyclohexane	180.0	.797	1.4408	.3312
Isoamylcyclohexane	194.0	.798	1.4420	.3316
<i>tert</i> -Amylcyclohexane	194.0	.8196	1.4520	.3291
<i>n</i> -Amylcyclohexane	202.0	.802	1.4428	.3304

TABLE C. AROMATIC COMPOUNDS

Compound	B. p., ° C.	$d_4^{20}$	$n_D^{20}$	S.R.
Benzene	80.112	0.87896	1.50123	0.33475
Toluene	110.68	.8669	1.49685	.33747
Ethylbenzene	136.15	.8669	1.49587	.3369
<i>p</i> -Xylene	138.40	.8610	1.49615	.33937
<i>m</i> -Xylene	139.30	.8641	1.49741	.33887
<i>o</i> -Xylene	144.05	.88011	1.50547	.33729
Isopropylbenzene	152.53	.8620	1.4922	.33668
<i>n</i> -Propylbenzene	159.45	.86214	1.4922	.33665
1-Methyl-3-ethylbenzene	160.0	.8690	1.4975	.33812
1-Methyl-4-ethylbenzene	162.4	.8619	1.4946	.33702
1-Methyl-2-ethylbenzene	164.9	.8826	1.5048	.33594
1,3,5-Trimethylbenzene	164.65	.8654	1.4992	.33945
1,2,4-Trimethylbenzene	169.18	.8762	1.5048	.33839
<i>tert</i> -Butylbenzene	168.9	.8669	1.4925	.33494

TABLE C. AROMATIC COMPOUNDS—concluded

Compound	B. p., ° C.	$d_4^{20}$	$n_D^{20}$	S.R.
Isobutylbenzene	170.5	.8666	1.4934	.33506
sec-Butylbenzene	173.50	.8623	1.4901	.3348
1,2,3-Trimethylbenzene	176.10	.8951	1.5139	.3363
1,2-Diethylbenzene	176.5	.8811	1.50347	.3358
1-Methyl-4-isopropylbenzene	176.8	.8571	1.4906	.3377
1,3-Diethylbenzene	180.55	.8617	1.4955	.3387
1,4-Diethylbenzene	182.5	.8623	1.496	.3388
n-Propyltoluene	183.2	.8604	1.4954	.3392
n-Butylbenzene	183.1	.86065	1.4900	.3379
o-Propyltoluene	184.0	.8739	1.4994	.3362
1,5-Dimethyl-2-ethylbenzene	185.5	.8740	1.5014	.3373
3-Phenylpentane	187.5	.8717	1.4969	.3356
tert-Amylbenzene	190.0	.8669	1.4929	.3362
sec-Amylbenzene	193.0	.8614	1.4906	.3360
1,2,3,5-Tetramethylbenzene	196.0	.8906	1.5104	.3360
Isoamylbenzene	198.5	.8586	1.4845	.3335

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## FORMIC ACID AS A SOLVENT FOR OZONIZATION INVESTIGATIONS<sup>1</sup>

BY RODGER M. DORLAND<sup>2</sup> AND HAROLD HIBBERT<sup>3</sup>

### Abstract

The use of formic acid as a solvent in ozonization investigations has been developed and its suitability demonstrated by experiments on organic compounds of known structure. This solvent shows a remarkable tendency to protect the aldehyde from oxidation to the carboxyl group. The stability of the aromatic nucleus to ozone is apparently somewhat greater in this solvent than in ethyl acetate.

### Introduction

The ozonization technique requires that the ozone-oxygen mixture be passed through a solution of the substance under investigation. The marked insolubility of the larger fractions of birch formic acid lignin (2) in the usual anhydrous, ozonization solvents such as chloroform and ethyl acetate renders them useless for this purpose. Glacial acetic acid is also found to be unsatisfactory in this respect. The similarity of formic to acetic acid, and the fact that lignin can be readily isolated by extraction with the former (2), suggested its use as an ozonization solvent. It was first necessary to compare its characteristics with those of a typical solvent such as ethyl acetate using a number of known compounds.

### Discussion

Maleic acid was chosen as a typical unsaturated compound. This yields on ozonization in various solvents primarily glyoxylic, and, secondarily, oxalic acid. In formic acid solution, glyoxylic acid was obtained in a yield of 98% and unaccompanied by any oxalic, as compared with one of 14.5% of the former and 80% of the latter, when ethyl acetate was employed in place of formic acid.

In connection with various oxidation studies relating to the structure of lignin (1) it was of interest to determine the stability of certain typical aromatic compounds towards ozone in formic acid and ethyl acetate respectively. It was found that vanillin on ozonization in formic acid could be recovered unchanged in 45% yield, no oxalic acid being formed in the reaction. Using ethyl acetate, vanillic acid was obtained in a yield of 21%; vanillin and oxalic acid were both absent in the reaction mixture. Similarly, veratric aldehyde

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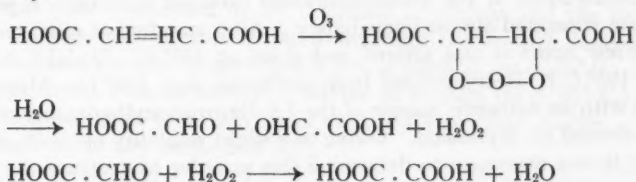
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on ozonization in formic acid gave no oxalic acid, and unchanged veratric aldehyde was recovered to the extent of 62%. With ethyl acetate as solvent, veratric acid was found in a yield of 45%, but no unchanged veratraldehyde. These results are summarized in Table I.

TABLE I  
FORMIC ACID AND ETHYL ACETATE AS OZONIZATION SOLVENTS

Product investigated	Formic acid solvent		Ethyl acetate solvent	
	Substance	Yield, %	Substance	Yield, %
Maleic acid	Glyoxylic acid	98	Glyoxylic acid	15
			Oxalic acid	80
Vanillin	Vanillin	45	Vanillic acid	21
Veratric aldehyde	Veratric aldehyde	62	Veratric acid	45

It is apparent that not only is the aldehyde group protected from oxidation in a formic acid medium but also the degradation of the aromatic nucleus is diminished. With maleic acid, oxalic acid formation is undoubtedly due, in part, to oxidation of the glyoxylic acid by hydrogen peroxide formed simultaneously.



Such an explanation, in view of the yield of hydrogen peroxide formed, accounts for the formation, however, of only a 50% yield of oxalic acid. The absence of oxalic acid formation in formic acid solution may be due to the fact that the acid used was not anhydrous (about 95% concentration), and thus the ozonide first formed could be decomposed immediately to form glyoxylic acid. It is known that hydrogen peroxide reacts with formic acid to give carbon dioxide, a fact that may explain the large percentage recovery of vanillin and veratric aldehyde when formic acid is used, the oxidizing effect of the ozone being exerted on the formic acid rather than on the products under investigation.

Formic acid may thus serve as a valuable and unique ozonization solvent, although its applicability will be limited to compounds that do not themselves react with it.

It will be noted that vanillin and veratric aldehyde undergo considerable decomposition on ozonization, but it should be borne in mind that these compounds are subjected to the action of the entire ozone used, there being no

ethylenic double bond to which the ozone can add. From this viewpoint vanillin and veratric aldehyde must be regarded as being comparatively stable under the conditions employed. The degradation when formic acid is used as the solvent is somewhat less than when ethyl acetate is used in this capacity. No oxalic acid is formed as a result of decomposition of the aromatic nuclei by the ozone.

### Experimental

#### *Ozonization of Maleic Acid in Formic Acid*

Two grams of maleic acid was dissolved in formic acid\* (35 cc.) and ozone (1.64 gm.) passed through the solution at 0° C. during a period of five hours. Upon completion of the ozonization the formic acid was removed under reduced pressure. The residual white solid dissolved on refluxing with 30 cc. of water. After cooling, it was filtered and diluted to 100 cc.

Absence of oxalic acid was shown by dilution of 3 cc. of the solution with 10 cc. of water and addition of 2 cc. of a saturated solution of calcium hydroxide. No precipitate or cloudiness was observed on standing. A series of tests with this reagent on solutions of oxalic acid of known concentrations showed that a definite precipitate was given by 0.0005 gm. of oxalic acid in 5 cc. of water.

Glyoxylic acid was determined as follows: 1.2 gm. of 2,4-dinitrophenylhydrazine and 80 cc. of water was heated to boiling and sufficient concentrated hydrochloric acid added to dissolve the hydrazine. To the warm solution was added 20 cc. of the above-mentioned ozonized solution. A yellow precipitate separated almost immediately. After standing at room temperature for a few hours it was filtered and dried at 105° C. Weight, 1.697 gm.; m.p. 195° C.† Recrystallized from methanol, m.p. 196° C. Mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of glyoxylic acid showed no depression. Owing to a slight solubility of the hydrazone in water it was necessary to determine this in order to evaluate the yield. A portion of the derivative (0.121 gm.) was added to a mixture of water (100 cc.) and concentrated hydrochloric acid (15 cc.) (under the same conditions as used previously) and the solution heated to boiling and allowed to stand at room temperature for a few hours. After filtration and drying, 0.073 gm. of undissolved material remained; this indicated that 0.048 gm. was soluble under these conditions. The theoretical yield of the 2,4-dinitrophenylhydrazone of glyoxylic acid from 2 gm. of maleic acid is 8.88 gm. Actually there was obtained 1.745 gm. (1.697 plus 0.048) from an aliquot of one-fifth of the total solution; this corresponded to a yield of 98%.

#### *Ozonization of Maleic Acid in Ethyl Acetate*

Maleic acid (0.5 gm.) was dissolved in anhydrous ethyl acetate (20 cc.), and ozone (0.57 gm.) was passed through the solution at 0° C. for a period of one and one-half hours. The solvent was removed, the resulting residue dissolved in water, filtered, and diluted to 25 cc. Calcium hydroxide solution

\* Schering-Kahlbaum formic acid, 95%.

† Melting points are uncorrected.

was added to a 5 cc. aliquot until there was no further precipitate. This precipitate was filtered, dried at 105° C. and weighed as calcium oxalate. Yield, 0.176 gm. corresponding to a yield of 80%. To another 5 cc. aliquot was added an excess of an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride. The precipitate was filtered, dried, and weighed. M.p., 197 to 198° C. Mixed melting point with the 2,4-dinitrophenylhydrazone of glyoxylic acid showed no depression. Weight, 0.064 gm., or a yield of 14.5%.

*Action of Ozone on Vanillin in Formic Acid*

Vanillin (1 gm.) was dissolved in formic acid (100 cc.) and treated in the usual manner with ozone (1.14 gm.). Removal of the formic acid from the pale yellow solution left a dark brown syrup which dissolved in warm water (150 cc.). This was filtered and diluted to 250 cc. Oxalic acid was absent.

A 25 cc. aliquot was diluted to 50 cc. with water and sodium acetate (3.5 gm.) and sulphuric acid (10%, 2 cc.) were added. The solution was warmed to 60° C. and to this was added water (10 cc.) at 60° C. containing *m*-nitrobenzoylhydrazine. After standing overnight the precipitated product was filtered and dried. M.p. 205° C. Mixed melting point with an authentic sample of the *m*-nitrobenzoylhydrazone of vanillin (m.p. 210 to 211° C.), 207° C. Weight obtained, 0.08642 gm., corresponding to 42% of the original vanillin. Another 25 cc. aliquot was extracted continuously with ether for 12 hr., the solution being dried and the ether removed under reduced pressure. The residue was sublimed at 12 mm. pressure and 100 to 110° C. The sublimate was then resublimed under the same conditions and the second sublimate carefully washed into a tared weighing bottle with anhydrous ether. Removal of the ether gave 0.04826 gm. of material, m.p. 76° C. The mixed melting point with an authentic sample of vanillin (m.p. 82° C.) was 81° C. This corresponds to a recovery of 48% of the original vanillin. The average value for the two methods is 45%.

*Action of Ozone on Vanillin in Ethyl Acetate*

One gram of vanillin was dissolved in ethyl acetate (100 cc.) and at 0° C. was subjected to the action of 1.08 gm. of ozone over a period of two hours. The solvent was removed under reduced pressure giving rise to a brownish oil which was dissolved in 125 cc. of warm water. The solution was filtered and the volume made up to exactly 250 cc. No precipitate of calcium oxalate was obtained with a portion of this solution upon the addition of calcium hydroxide solution. A 100 cc. portion of the reaction solution was continuously extracted with ether for 18 hr. and the solvent removed. Sublimation of the residue at 10 mm. and 100° C. gave only a minute quantity of oil, but at 140° C. a yellowish-white crystalline material was obtained, m.p. 197 to 198° C. Two recrystallizations from water yielded a white crystalline product, m.p. 206 to 207° C. A mixed melting point with an authentic sample of vanillic acid showed no depression. From a further 60 cc. portion of the solution 0.0563 gm. of sublimate was obtained, corresponding to a yield of 21%.

*Action of Ozone on Veratric Aldehyde in Formic Acid*

Freshly distilled veratric aldehyde (1 gmf., m.p. 45 to 46° C.) was dissolved in 90 cc. of formic acid and treated with 0.64 gm. of ozone at 0° C. for one hour. Removal of the solvent left a brown syrup which was dissolved in warm water, filtered, and diluted to 250 cc. No oxalic acid was obtained. A 50 cc. aliquot was diluted with 2% acetic acid (100 cc.), warmed to 60° C., and water (25 cc.) at 60° C. containing *m*-nitrobenzoylhydrazine (0.3 gm.) added. After standing overnight the precipitated product was filtered and dried; m.p. 213 to 214° C.; after recrystallization from methanol, 222 to 223° C. mixed melting point with an authentic sample of the *m*-nitrobenzoylhydrazone of veratric aldehyde (m.p. 224 to 225° C.), 223° C.; weight, 0.2470 gm., corresponding to a recovery of 62% of the veratric aldehyde.

*Action of Ozone on Veratric Aldehyde in Ethyl Acetate*

Pure veratric aldehyde (1 gm.) in ethyl acetate (90 cc.) was treated similarly with 1.30 gm. of ozone over a period of two hours. Removal of the solvent left a brown syrup which was dissolved in water, filtered, and diluted to 250 cc. To a 50 cc. aliquot was added 2% acetic acid (100 cc.) and *m*-nitrobenzoylhydrazine (0.3 gm.) in the manner already described. Weight of hydrazone obtained, 0.0060 gm., indicating a negligible amount of veratric aldehyde present.

A 100 cc. aliquot of the reaction solution was evaporated to dryness under reduced pressure and the residue sublimed at a pressure of 0.008 mm. and at 135° C. The crystalline material (0.1974 gm.) was recrystallized from water giving a white crystalline product, m.p. 177° C.; mixed melting point with an authentic sample of veratric acid (m.p. 181° C.), 180 to 181° C.; yield, 45%.

### References

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